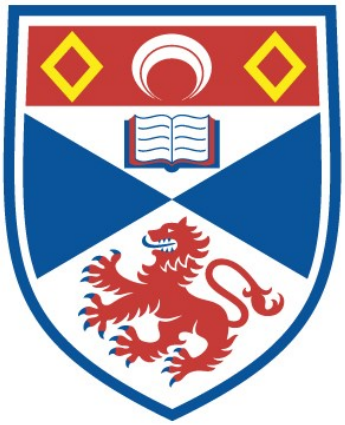
THE SOLUBILITY OF GASES IN AQUEOUS ALCOHOLS

Robert Wilson Cargill

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE SOLUBILITY OF GASES IN AQUEOUS ALCOHOLS

by

ROBERT WILSON CARGILL, B.Sc., A.R.I.C.

A thesis presented to the
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I N D E X

Page

Chapter 5 DISCUSSION OF RESULTS

DECLARATION

I hereby declare that the following thesis is a record of work carried out by me, that it is my own composition, and that it has not been previously presented for a higher degree.

The investigation was carried out in the Chemistry Department of Dundee College of Technology, under the supervision of Dr. T.J. Morrison, then Mr. N.B.B. Johnstone, and of Dr. C. Horrex of the University of St. Andrews.

CERTIFICATE

I hereby certify that Robert Wilson Cargill has spent nine terms at research work, as a part-time student, under my supervision, that he has fulfilled the conditions of Ordinance General No. 12 (St. Andrews), and that he is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

UNIVERSITY CAREER

I entered the University of St. Andrews in October 1958, and graduated with First Class Honours in Chemistry in June 1962.

The next two years were spent in industry where I was concerned with research into glasses and enamels, and following this I was admitted to the Associateship of the Royal Institute of Chemistry.

In October 1964 I accepted my present lectureship in the Chemistry Department of Dundee College of Technology.

In June 1969 I was admitted as a part-time research student of the University of St. Andrews, with two terms per year credited to my period of study. From then until February 1974 the work described in this thesis was carried out.

ACKNOWLEDGEMENTS

It is my pleasure to record my appreciation to the following people, without whose assistance this thesis could not have been submitted.

Dr. T.J. Morrison, who introduced me to the interesting and intriguing field of gas solubilities, stimulated me with his spirit of enthusiasm and enquiry, and acted as my supervisor until June 1971, when his untimely death robbed me of an adviser and friend; I am also indebted to him for the use of some of his data in this thesis;

Mr. N.B.B. Johnstone, who acted as my supervisor from June 1971 and enabled my work to proceed;

Dr. C. Horrex, my University supervisor, whose encouragement stimulated the initiation and completion of this project, and who first showed me the elegance of the thermodynamics I have used;

the Governors of Dundee College of Technology, who provided laboratory facilities, and also some financial assistance;

Miss Ann Ramsay, whose meticulous typing and cooperation facilitated compilation of the thesis;

the Reprographic Unit of the College which produced photographs and diagrams;

and my wife, Isobel, whose forbearance and understanding made all the work more of a pleasure and less of a burden.

SUMMARY : ABSTRACT OF THESIS

Extensive measurements have been made of the solubilities of the five gases helium, hydrogen, argon, oxygen, and carbon dioxide, in ethanol/water and in t-butanol/water mixtures over the whole of their concentration range, and throughout the temperature interval 4°C to 61°C. The measurements were carried out by the less usual flowing-film technique, which has been described in detail. It depends on the rapid establishment of equilibrium between a gas and its solvent while the liquid flows in a stable, thin film down the walls of a tube enclosing the gas. Results were reproducible, corroborated at relevant points by results obtained by other workers from the other more common mixing techniques.

These solubility measurements were used to investigate the effects of foreign molecules on the structure of liquid water. To this end standard thermodynamic functions were calculated for each of the solubilities, having programmed a computer to carry out the arithmetic. Graphs were drawn to show the relationship of the functions to the gas dissolved, the alcohol mixed with the water, and the temperature. Most information was obtained from the enthalpy and entropy changes in the systems, and certain features of their dependence on the concentration of the alcohol.

A mixture model for water structure has been described, and some aspects of it elucidated. The size of any molecule introduced into water has been shown to be an important factor in its influence on the water structure. A quantitative estimate has been made of the effect of

temperature on the mole fraction of water molecules which are completely hydrogen-bonded, called "icebergs" or "clusters". An estimate has also been made of the relative amounts of different-sized clusters at various temperatures, and it has been concluded that as the temperature rises, there is a selective and progressive destruction of the largest clusters.

Finally, a mechanism has been suggested for the stabilisation of clusters by added solute molecules, which depends on their efficiency at preventing thermal disruption of the clusters.

CHAPTER 1 GAS SOLUBILITIES

1. INTRODUCTION

The solubility of gases in liquids has been investigated quantitatively since the beginning of the last century. The classic work of Henry[1], reported in 1803, was the first attempt to correlate some of the factors involved.

Since then, much progress has been made, in the variety of solute-solvent systems studied, in the accuracy of the experimental results, and, for some systems, in the theoretical interpretation of the data.

(a) The variety of systems studied

A recent review by Battino and Wilhelm[2] tabulates reliable data on the solubility of 16 different gases in 39 different solvents. This list excludes water and aqueous mixtures, which an earlier review by Battino and Clever[3] does cover briefly.

Solubility of gases in aqueous mixtures is, however, of special interest, both for investigations into the structure of liquid water itself, and for the unique and important role that these mixtures have in biochemical fields.

The present investigation has been concerned with such three component systems. Aqueous ethanol and aqueous tertiary butanol, over practically their whole concentration range, were both used as solvents for the gases hydrogen, helium, oxygen, argon, and carbon dioxide, at atmospheric pressure and over the temperature range 5-60°C.

(b) Experimental results

The different techniques which have been used to obtain reliable data are also reviewed by Battino and Clever[3]. The one employed in this work gives results which are reproducible within about 0.5%. The technique was devised by Morrison[4], and basically it consists of the saturation of a solvent with gas while the liquid flows in a thin film down the walls of a glass tube. Such a flow system is a useful alternative to the more usual batch method involving shaking or stirring, although some more modern versions of the latter seem capable of somewhat greater accuracy.

(c) Solution theories

Some solutions can be described in terms of the concepts of ideality[5] and regularity[6], but none in which water is a component can be so described.

Thus complete theoretical explanations are still unavailable for aqueous solvents. Nevertheless a comparison of the thermodynamic functions, calculated for the solubilities measured, does give some indication of parameters which may be relevant to the problem.

2. SOLUBILITIES OF GASES IN LIQUIDS

(a) Liquid solvents

Hildebrand, in the fourth edition of his textbook on solutions[7], points out the usefulness of gases as tools for theoretical studies on the liquid state. By means of these, the intermolecular forces within non-polar liquids have been investigated with some success. Polar liquids, however, and particularly water, have presented a more intractable problem. This is all the more intriguing and challenging when the ubiquity of water is recognised, along with its impact on marine and biochemistry, and with its intrinsic theoretical and structural interest.

So whilst water has been used as a solvent from prehistoric times, and whilst chemists of the last century measured the solubility of gases in it, yet in its theoretical aspects it still lags behind much less common liquids, which of course possess much simpler molecular structures, and more easily described molecular interactions in the liquid state.

(b) Gaseous solutes

The simplest gaseous solutes are the noble gases. The first complete investigation of the solubility of these gases in water, over substantially the whole of the liquid range of water, was carried out by Morrison and Johnstone[8] using the flowing film technique. Their results confirmed and extended those of Lannung[9] (who also measured the solubility of these gases in six organic solvents). Since then results have been published by some other

workers, but mostly for argon over a shorter temperature range; these data are 1-2% higher, and were summarised in a paper by Smith *et al*.[10] in 1968.

Morrison and others[11-13] also measured the solubilities of other gases in water and in aqueous solutions of electrolytes to study the "salting-out" effect, whereby the solubility of a gas in water is noticeably decreased by the addition of a salt. Hydrogen, nitrogen, oxygen, carbon dioxide, methane, ethane, propane, n-butane, ethylene, carbon tetrafluoride, and sulphur hexafluoride were each used as solute, and some trends in their salting-out were noticed with a variety of salts. It was found possible to fit the solubility data to an empirical equation proposed by Valentiner[14], of the type

$$\log s = -a + b/T + c \log T$$

where s = volume of gas at S.T.P. dissolved by 1 kg of solvent,

T = temperature,

and a, b, and c are constants which are functions of the systems in question. They are in fact directly related to the thermodynamic functions of the equilibrium, viz. partial molal entropy, enthalpy and heat capacity changes. (See Appendix I.) The relative magnitudes of these parameters were qualitatively related to some current theories of solubility mechanisms.

(c) Solvent mixtures

Ben Naim and coworkers have studied the effect of the addition of both electrolytes and non-electrolytes on the solubility of argon in water.[15-18] They interpret their results in terms of a two-structure model for liquid water. This is briefly that the

equilibrium between an ordered ("iceberg") and a disordered (more dense) form of the fluid is shifted in the presence of solute molecules.

Using some simple salts such as the alkali metal halides,[17] they obtained results similar to those of Morrison and Johnstone. Their results with tetraalkyl ammonium salts[18] are also similar, although of lower accuracy, and cover a smaller temperature range.

Aqueous solutions of non-electrolytes have been studied by them in more detail. Results have been reported and analysed for the aqueous methanol,[19] ethanol,[20] ethylene glycol,[21] and p-dioxan[22] systems. The effect on the solubility of argon of increasing the mole fraction of the organic components of the solvent is interpreted in terms of modifications to the structure of water induced by both the gas and the non-electrolyte: in these ternary systems, one component can be used as a probe to monitor the effect of the other. This has been the basis for several theoretical studies on water structure,[23] such as are described by Ben Naim in recent reviews in text books on Water.[24,25]

At certain points this approach leads to conclusions similar to those reached by Franks *et al.* who have studied some physical properties of aqueous alcohol mixtures,[26] using the propanols and t-butanol as well as methanol and ethanol. These have included the alteration of the surface tension[27] and of the temperature of maximum density[28] of water by the addition of small quantities of these alcohols. The enthalpy and entropy changes on mixing also lend support to the same kind of mixture model: the more dilute solutions of the alcohols are again most adequately explained.[29]

Other work on the solubility of gases in aqueous non-electrolyte solutions is more fragmentary. At the one temperature of 30°C, the solubility of oxygen over the full range of concentrations of aqueous methanol, ethanol, 1- and 2-propanols, 1-butanol, ethylene glycol, and glycerol has been measured[30] Even more limited results have been reported on the solubility of nitrogen and oxygen[31] and of carbon dioxide[32] in aqueous ethanol, and of oxygen in aqueous methanol[33]

(d) Objectives of the present investigation

Argon is the only gas which has been used as solute in most other studies of structural modifications of water by certain non-electrolytes, and at temperatures of 5-25°C. Fairly detailed theories have been built upon this rather limited range of evidence, and this suggested the following lines of investigation.

(i) It seemed desirable to find out whether the gas argon was unique or typical in its behaviour, and if in fact it was the most sensitive probe to use in these structural investigations. Thus gases of fairly diverse characteristics were chosen as solutes, viz.

(a) helium and argon, both noble gases but whose atom sizes are different, i.e. 190 pm and 288 pm respectively in diameter;

(b) hydrogen and oxygen, which may have some electronic interaction with water, and whose molecules are both diatomic yet compare in size with the atoms of helium and argon respectively, i.e. 240 pm and 298 pm for their respective molecular diameters;

(c) carbon dioxide, which does have a definite interaction with water both physically and chemically: its molecular diameter is 334 pm. (All values from viscosity determinations.[34])

A comparison of how each of these gases dissolves in a given aqueous mixture was therefore undertaken. The data will be useful for the evaluation of theories of aqueous solutions which may yet be proposed, as pointed out by Ben Naim;[19] and in their own right are valuable in opening up hitherto unexplored regions of interest.

(ii) The temperature range was extended to cover 5-60°C, in order to increase the reliability of some of the thermodynamic data, and to extend its applicability.

(iii) Aqueous ethanol and aqueous t-butanol were chosen as solvents. Some aspects of the solvent properties of aqueous ethanol have already been reported, and it may be regarded (rather than methanol) as a "typical" alcohol. No work on t-butanol however has been reported in this field. It is the highest alcohol which is completely miscible with water in all proportions, it has a much bulkier alkyl group than ethanol, and its marked influence on water as solvent at certain low concentrations has already been noticed.[35] In fact, Arnett says, "If we wish to amplify the extrema behaviour of alcoholic binaries, we will use t-butyl alcohol as one of the components."[36]

A comparison was made of how each alcohol changed the solubility in water of a given gas.

This work has implications in biological and medical fields of current interest. The understanding of aqueous protein solutions, and of the conformational stability of nucleic acids, has been aided by studies on solutions of nonpolar and mixed solutes, using the concept of hydrophobic bonding.[37,38] A theory of the mechanism of anaesthesia, due to Pauling,[39] depends on a solute-ordering effect produced in nerve tissue by the anaesthetic molecule.

Thus some ideas about the normal and abnormal functioning of physiological and biochemical processes might be obtainable from this kind of investigation.

CHAPTER 2 EXPERIMENTAL TECHNIQUES

1. HISTORICAL

A comprehensive review by Markham and Kobe[40] in 1941 describes in detail what might be termed the more historical techniques of solubility measurement, whilst a review by Battino and Clever[3] in 1966 describes techniques capable of greater accuracy.

(a) Early methods

(i) Henry[1], Bunsen[41] and Ostwald[42] to mention some of the notable contributors to this field in the nineteenth century, each used modifications of the same technique, viz. the measurement of the volume of a gas before and after it had been brought in contact with a given quantity of gas free solvent. The gas was usually mixed with the solvent by shaking, and various means were used to introduce the gas and measure its volume.

Ostwald introduced the most significant improvement by connecting to the absorption vessel a burette to measure the gas volume, instead of using the vessel itself for this. This apparatus was in turn modified by introducing various types of flexible joints, although Lannung[9] in 1930 assembled all parts of the apparatus on one rigid frame to be shaken until equilibrium was reached.

(ii) A different technique involved the measurement of the volume of gas extracted from a given volume of saturated solvent. This was used most frequently for the analysis of naturally occurring solutions, e.g. sea water and blood. The gas was extracted by boiling or by pumping accompanied by agitation. The apparatus of Van Slyke,[43] still in use in many biochemical laboratories, is a good example of this.

(iii) Chemical methods were used for some few gases, e.g. oxygen, chlorine, hydrogen chloride, ammonia, and sulphur dioxide, where titrimetric analysis could be applied with reasonable accuracy.

(b) Sources of error

From the technical viewpoint, the original Ostwald type of apparatus may have given rise to errors due to difficulties of construction. For example the gas might be in contact with flexible connections (which might leak), the control of pressure and temperature might not be adequately sensitive, the shaking of a large apparatus is difficult, and the presence of mercury is undesirable with certain gases. Again, many errors were almost certainly due to impurity of materials, including the use of solvent which was not completely gas free.

The main source of error, however, was failure to attain equilibrium, either by unsaturation of the solvent due to incomplete mixing, or by its supersaturation caused by too vigorous shaking[44] and excess pressure due to a hydrostatic head in the liquid.[45]

Uncertainty also exists about the allowances to be made for solvent vapour which will increase the volume of dry gas introduced, or, if the gas is presaturated with solvent vapour, solvent may condense in cooler parts of the apparatus rendering pressure control difficult, and producing a change in gas composition. These points were discussed by Horiuti.[46]

2. MODERN TECHNIQUES

(a) Special methods

Mass spectrometry and gas chromatography have been used successfully to measure the solubility of certain gases in certain solvents. The former method has particular relevance to isotope effects,[47] whilst the latter has been applied best to the determination of the solubilities of hydrocarbons.[48]

Specialised techniques have been applied to work at high pressure,[49] and high and low temperatures, e.g. solubilities of gases in molten salts,[50] and in liquid hydrogen.[51]

(b) Batch methods

Several modern versions of the Ostwald technique, capable of a very good precision, have been used recently, now that a full appraisal has been made of the factors affecting accuracy. More thorough degassing of the solvent is standard procedure, closer control over variables is exercised, and shaking has largely been replaced by magnetic stirring or electrical pumping. Correspondingly the apparatus has become more complex and expensive.

Equilibration by stirring has been used by Burrows and Preece (1953) to determine the solubility of helium in oils;[52] by Friedman (1954) for sulphur hexafluoride in water and nitromethane;[53] by Ben Naim (1963) for his work on argon in solvent mixtures[54] already referred to in chapter one; and by Smith *et al.* (1968) who developed their apparatus specially for the fluorinated gases which are very insoluble in water.[10]

Shaking or rocking by mechanical means has been preferred by Cook and Hanson (1954) whose apparatus[55] has been recommended for its capability of the high precision of 0.05%. It was also used by Hildebrand and Reeves[56] (1957), by Klots and Benson (1963) for work on sea water as solvent when 48 hours was allowed for equilibration;[57] and by Scholander[58] (1947) and Douglas[59] (1965) whose methods are on the micro scale.

Pumping, recycling, and flow of a liquid film are all incorporated by Hildebrand and Dymond (1967) in their method for measuring the solubility of the noble gases in cyclohexane.[60]

(c) Flow methods

The original apparatus employing the flow of a thin film of solvent down the walls of a tube enclosing a given volume of gas was described in 1948 by Morrison and Billett.[4] It has been modified in some respects by Morrison (see reference 12) and also by the author, and will be described in detail in the following section.

Also, however, Clever and co-workers;[61] and Saylor and Battino[62] in 1957-58, and Koenig[63] in 1963, have used this method (with their

own minor modifications), to measure, for example, the solubility of noble gases in hydrocarbon solvents.

3. THE FLOWING FILM TECHNIQUE

(a) Accuracy of solubility measurements

In the design and operation of the apparatus to be described, the following are the main factors to be controlled.

(i) *Equilibration of gas with solvent*

The unique feature of this technique is the manner in which equilibrium is achieved between the gas and its solvent, i.e. by a thin flowing film of liquid which is capable of rapidly dissolving the gas with which it is in contact.

The original apparatus is shown in Figure 1. A volume of gas, saturated with solvent vapour at the temperature of the experiment, is enclosed in an absorption tube A, which also acts as a gas burette. Into this is run dropwise from X a slow and steady stream of solvent whose mass can be measured as it drops from Y, and recorded against the simultaneous change in gas volume. B is a levelling tube to maintain pressure control on the gas.

So that equilibrium is reached, however, the solvent film must be stable, free from turbulence, and expose adequate surface area. Stability of the film is ensured by using clean glass surfaces (steeped in "Decon" and thoroughly rinsed with distilled water), and a drop rate high enough to prevent them from partial drying (not less than 25 g of

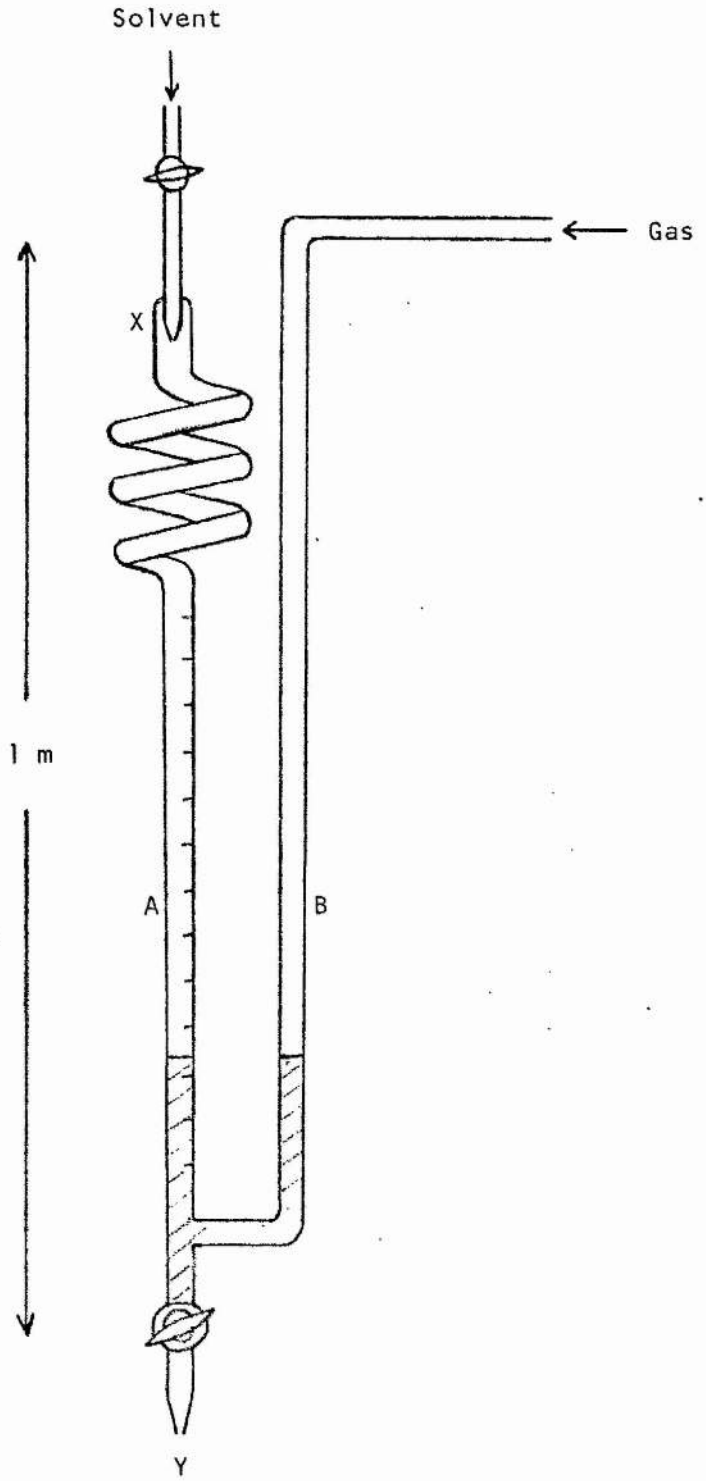


Figure 1 : SIMPLE GAS ABSORPTION BURETTE

solvent per hour). Conversely the film becomes turbulent and inefficient at flow rates which are too high, and not more than 100 g per hour is normally used. The effective area of the film depends on the tube dimensions, but mainly on its length which should be about 600 mm. The inside diameter is normally 8-10 mm, although in one modified design of the apparatus this was increased to 17 mm. With larger diameters, it is difficult to ensure that the film covers the whole circumference of the tube.

These points became clear after an attempt was made to reduce the apparatus by a factor of 10 to semi-micro scale. Absorption tubes about 150 mm long and of diameters up to 20 mm were used, empty and with various kinds of packing (capillary tubes, beads, and helices of glass). None of them, even at low flow rates, gave more than 90% saturation as tested on standard systems. Subsequently using a column of variable length, it was found that this parameter should be at least 500 mm, even with a spiral on top. It is thought that the function of the spiral is to impart a swirl and spread to the film as it enters the vertical tube, rather than achieve much solution of the gas.

(ii) *Measurement of solvent mass and gas volume*

There is no difficulty in measuring the mass of solvent which collects from the bottom of the absorption tube. A total mass of 200-700 g (depending on the gas solubility) is collected, and using a top-pan balance an accuracy of ± 0.5 g is easily obtainable.

The volume of gas dissolved is obtained from measurement of the volume of gas left in the apparatus, which is of the order of 100 cm^3. Burette readings are recorded to ± 0.02 cm^3. The accuracy of the volume measured, however, depends on the control of temperature and pressure.

Temperature is controlled to ± 0.05 K by the use of a thermostatted water bath. This control is also essential because of the temperature coefficients of the solubility of the gas, and of the vapour pressure of the solvent which saturates the gas.

Pressure is controlled (at about 1 atmosphere) by operating a manometer arrangement at the gas reservoir. Up to 7 hours may be taken to complete a determination of solubility. During this period, the barometric pressure must be observed (a barograph was found useful) and any changes compensated for by raising or lowering the manometer. A variation in pressure of only 1 mmHg gives an error in the volume of 80 cm^3 of about 0.1 cm^3. The volume of gas dissolved is usually 5-25 cm^3, so for low solubilities especially, this pressure control is very important. The total pressure of the gas in the apparatus over the period of the experiment must therefore be kept constant, although its magnitude need not be recorded since Henry's law is obeyed within the limits of the experimental conditions.

(iii) *Preparation of gas-free solvent*

The original procedure used by Bunsen was simply to boil the solvent. More modern methods involve boiling under vacuum with the accompanying loss of about 20% of the solvent,

pumping on the frozen solvent for 3 cycles of at least an hour each, or spraying boiled solvent through a fine nozzle into an evacuated flask.[62] It seems that these methods can completely degas a solvent.

Buchanan,[64] however, tested for the extraction of carbon dioxide from water by distillation, and found that a barium hydroxide test was negative after a quarter of the distillate had passed over. Others like Leduc[65] found that boiled distilled water still gave up gas bubbles on freezing, and successive freezing in vacuo did not completely free it from gas.

Our apparatus uses an adaptation of the original method, based on the vapour-pump principle. It is described in reference 12 and illustrated in Figure 2. Solvent is thoroughly boiled in a glass flask, and by the vapour pumping through a glass tube, gas-free solvent collects in an inner reservoir from the bottom of which it is syphoned off into the absorption tube as required. This boiling and pumping seems to remove substantially all of the gas from the solvent. The method commends itself for its simplicity, and although it has been criticised, the accuracy of the results obtained seems to indicate that much less than 1% of the gas is left in the solvent.

(iv) *Purity of the materials*

The gases hydrogen, helium, and argon were obtained from British Oxygen Company cylinders and were stated to be more than 99.9% pure; oxygen from the same source was stated to be more than 99.5% pure. Carbon dioxide was prepared by

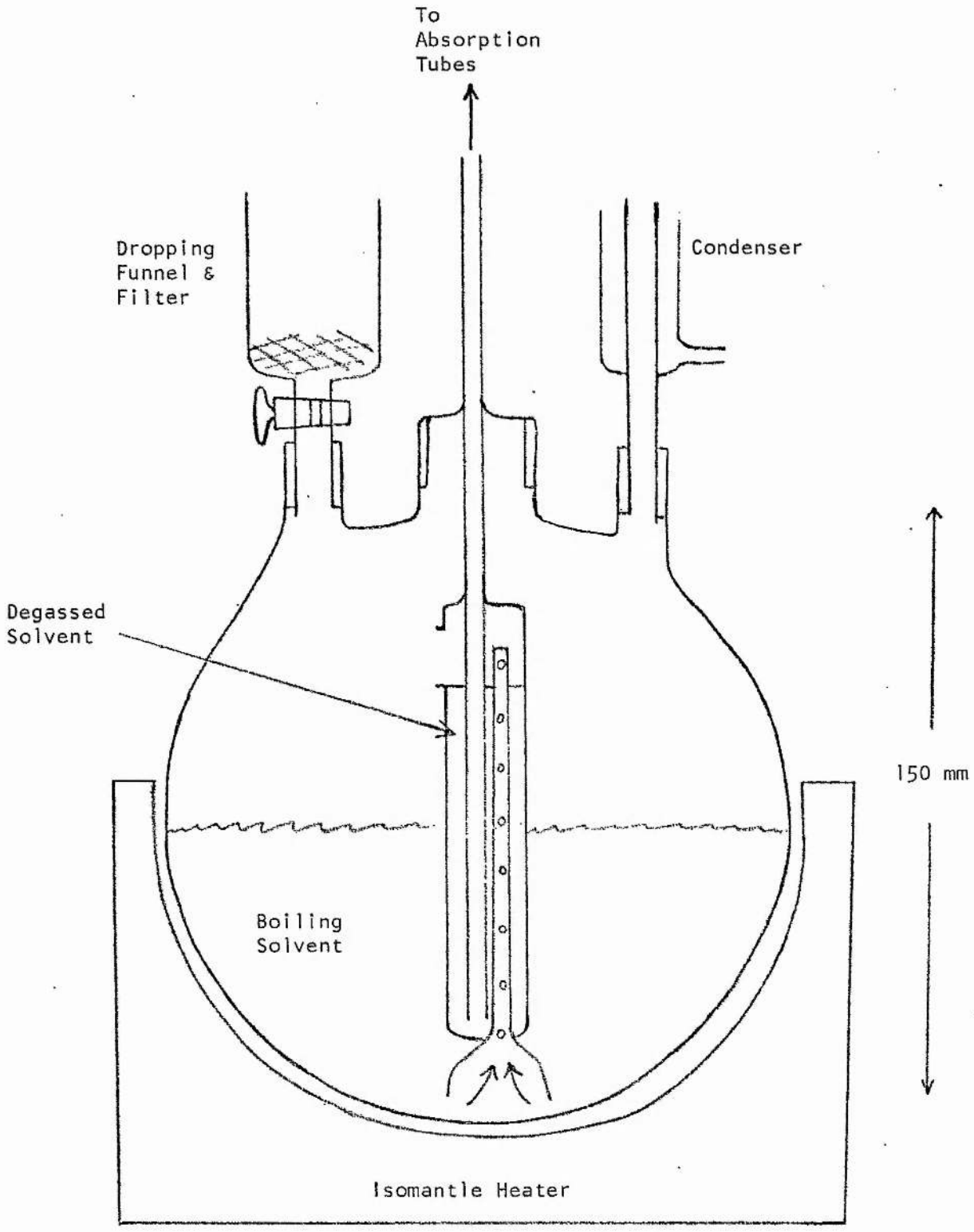


Figure 2 : VAPOUR PUMP FOR DEGASSING SOLVENT

the action of dilute hydrochloric acid on marble chips, and was estimated to be more than 99% pure.

Deionised water, absolute ethanol (spectroscopic grade for the very dilute solutions), and reagent grade t-butanol (98% boils between 82°C and 83°C) were used in the various experiments. Mixtures of water and the alcohol were made up and their densities measured at 20°C. From data in International Critical Tables, Vol. III p.112, and 117-118, their exact compositions were obtained. Densities were also checked after every determination, and any small loss of the more volatile component was made up.

(b) Description of the apparatus used

The original apparatus was modified by Morrison, as described in reference 12, by separating the gas burette from the absorption tube. This arrangement is more adaptable to widely different solubility measurements, ensures a constant length of solvent film in the absorption tube, and allows easier filling with solvent on completion of a run. Thus the tube is kept wet, which is important for repeated usage. In this form it was constructed and used by the author, and is shown in Figure 3.

The absorption and measuring section is mounted through a rubber bung in the lower end of a thick pyrex-glass pipe, 1 m long and 75 mm inside diameter. Water at constant temperature is pumped to the bottom of this pipe by a "Circotherm" unit immersed in a reservoir tank level with the top of the tube, whence it returns by a syphon overflow system. Water is circulated at a rate

sufficient for temperature control to ±0.05 K as recorded on a thermometer totally immersed in the bath alongside the absorption tube A.

Gas is stored over brine in a reservoir D of about 400 cm^3 capacity. This brine is previously boiled out and allowed to cool in contact with the gas which is then fed into the reservoir from the supply cylinder by displacement of the brine.

Solvent is filled into the boiler flask through a glass-wool filter, and it is recycled after use. It enters the apparatus by a gravity feed through drawn capillary jets controlled by taps. The initial filling with solvent is carried out by opening tap X, then after the absorption tube A is full and overflows into the burette B, tap W is opened to fill up tube C. This solvent (with air now dissolved in it) and the remaining air in the apparatus are swept out by a thorough flushing with the gas to be used, through to exit taps Y and Z, having closed W and X. The apparatus is now ready for use and only needs purging when the solvent is changed. It is filled with solvent by closing taps Y and Z, and allowing solvent to run in from X.

A measurement of solubility is carried out as follows.

The thermostat pump and heater or refrigeration unit are switched on so that the temperature becomes constant as required. Solvent is boiled in the flask and collects continuously in the inner reservoir.

Keeping the gas near atmospheric pressure, the solvent in the apparatus is drained from tap Y and then tap Z, until by syphoning

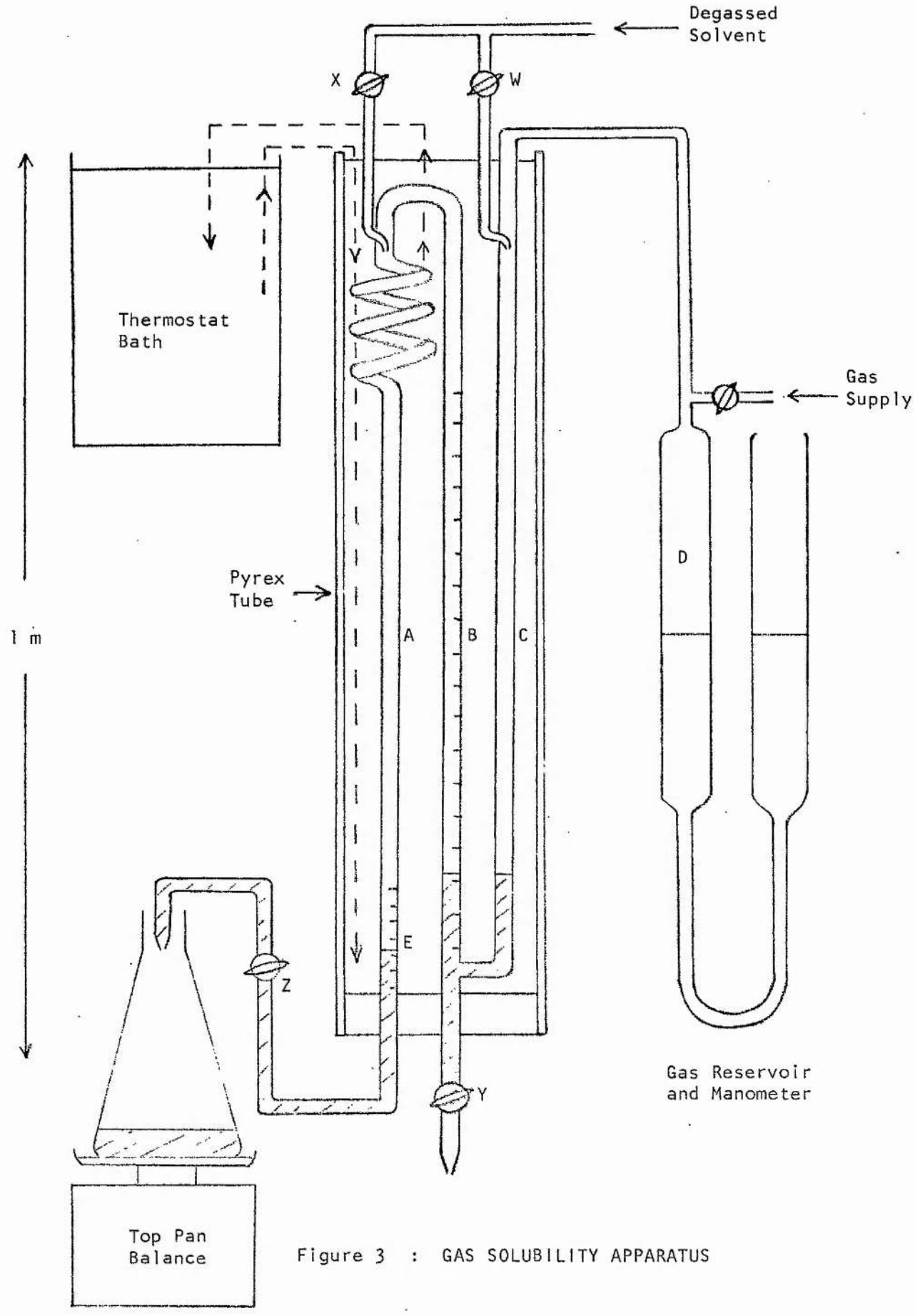


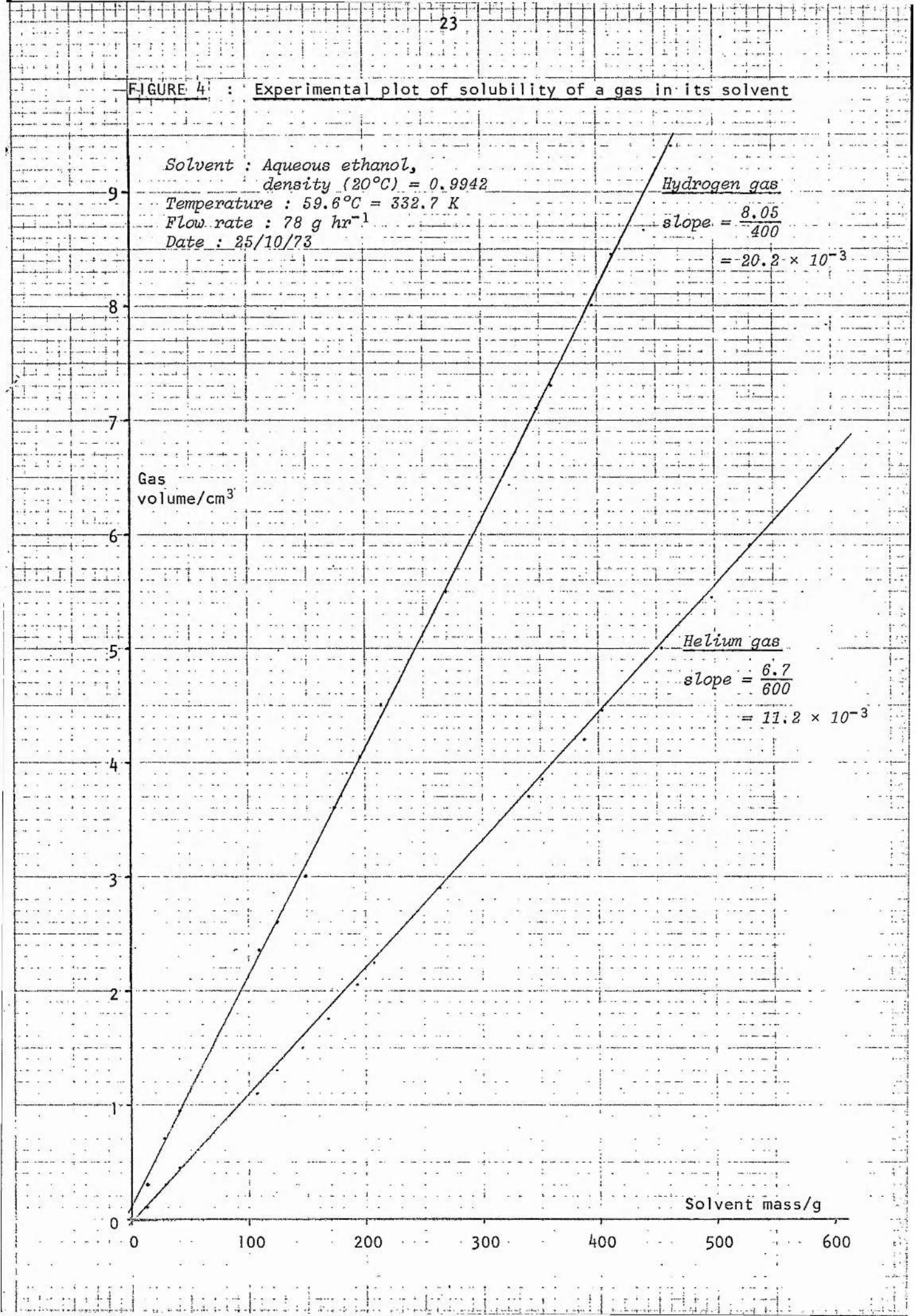
Figure 3 : GAS SOLUBILITY APPARATUS

into the receiving flask on the balance, it steadies on a reference mark on scale E. At the same time, taps X and W are opened to allow degassed solvent to enter the tubes, drop by drop at a fixed rate. From X it flows down the absorption tube in a thin film before passing over into the weighing flask. From W it runs down the levelling tube C where it also becomes saturated with gas at the temperature of the experiment, and collects in the bottom of the burette and levelling tube. In this way it seals off into the burette and absorption tube a volume of gas already saturated with solvent vapour. This is the volume which changes as the gas is dissolved, so that the drop rate from W is adjusted to keep the same liquid level in tubes B and C, ensuring constant pressure of the gas in the apparatus.

As the gas dissolves the solvent level rises in the burette. Simultaneous readings are taken on the balance, the zero reference scale, and the burette, and are repeated at fairly regular intervals throughout a period of about 5 hours, or until enough gas has been dissolved. Pressure fluctuations and compensations cause the zero reference mark to change, e.g. if the barometer shows a pressure drop of 1 mmHg, the gas reservoir side arm is manually raised by 12 mm (since the densities of mercury and brine are in the ratio of 13.6:1.1), and the zero mark falls by about 14 mm. When this occurs, a correction has to be applied into the calculation of the changes in gas volume and solvent mass : see the data collection sheet in Appendix II.

The most convenient treatment of the results is plotting a graph of the volume of gas dissolved against the simultaneous mass of solvent collected. Drawing the best straight line through these

FIGURE 4 : Experimental plot of solubility of a gas in its solvent



points (about 15) helps to smooth out experimental errors (mostly due to pressure fluctuations) as shown in Figure 4. The slope of this line gives the solubility of the gas at the temperature of the determination with an accuracy of ± 0.1 cm^3 in the volume of gas dissolved. Another benefit of this graphical treatment is that any curvature of the line indicates impurities in the gas or solvent, and this can be rectified.

Generally it may be observed that the longer a run is, the more reliable are the results. It was found, however, that for most systems enough gas had dissolved in about 5 hours. For the very insoluble gases, this time could easily be extended.

(c) Modifications to the apparatus

For maximum reliability, it is important that a slow and steady flow of solvent is maintained in the absorption tube throughout the period of the measurement. This was difficult to control by standard glass taps, so that these were first of all replaced by stainless-steel needle valves. The control of the flow rate was better, but it tended to slow down over the period of a run, probably due to dust particles collecting at restrictions. Rather than introduce elaborate filters which themselves would clog up and hinder the passage of solvent, it was decided to replace valve X by a pump.

The pump used was by Watson-Marlow, shown in Figure 5. It has a variable speed and gives a constant flow rate for long periods of time. A flexible tube, laid across a curved anvil P, is squeezed by an advancing roller so that its contents are pushed forward at a steady rate. If the bore of the tube is too large, a peristaltic

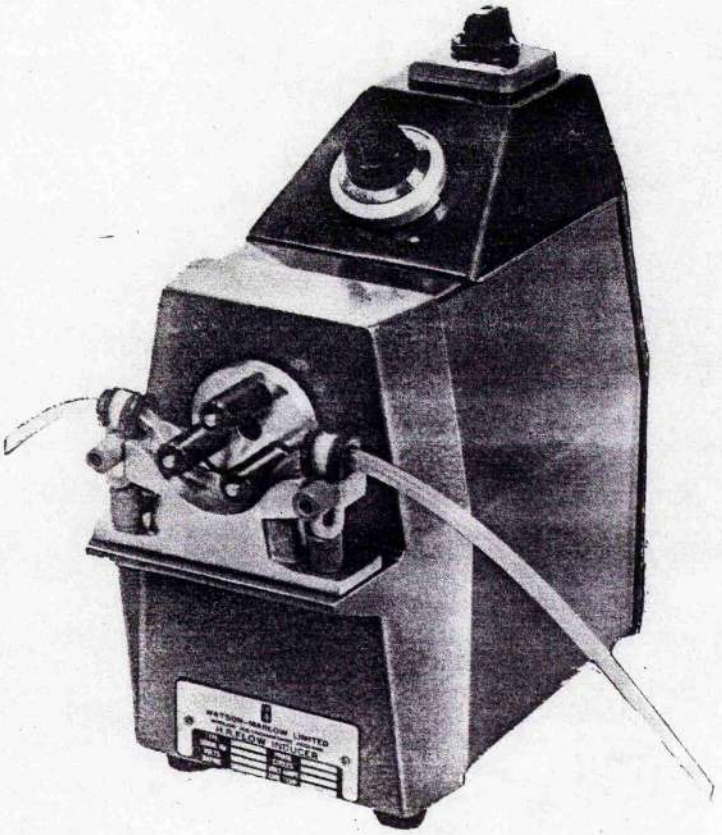


Figure 5 : WATSON-MARLOW PUMP

flow results. This was a disadvantage since the absorption film has to be fed steadily. By reducing the bore to 0.8 mm, the drop rate of solvent was found to be satisfactory and constant.

The flexible tubing material is critical. Silicone rubber was tried first, but results were not reproducible. This was due to the permeability of silicone rubber to gases of the atmosphere which were contaminating the solvent as it passed through this tube. Separate tests confirmed this, but also showed that butyl rubber and neoprene tubing were satisfactory. Both of these materials have been used. (In the gas feed system P.V.C. tubing was also used at one time to make the construction easier, but results were again unreliable. Glass had to be used throughout since especially the noble gases can penetrate plastic and most rubber tubing.)

After some considerable experience had been gained in the manipulation of the apparatus, it was realised that the output of results could be doubled by adding a second set of solubility tubes.

The same thermostat reservoir and pump were used to supply a second glass pipe (alongside the first) containing the other solubility section. The same solvent system fed a second piece of tubing laid across the anvil P and a second control valve W, to enter the other set of tubes. Different gases were then led in to each section, so that during a single period, measurement could be obtained of the solubility of the two gases in the same solvent at the same temperature. See Figure 6 for a block diagram of this arrangement, which was used for all the work done

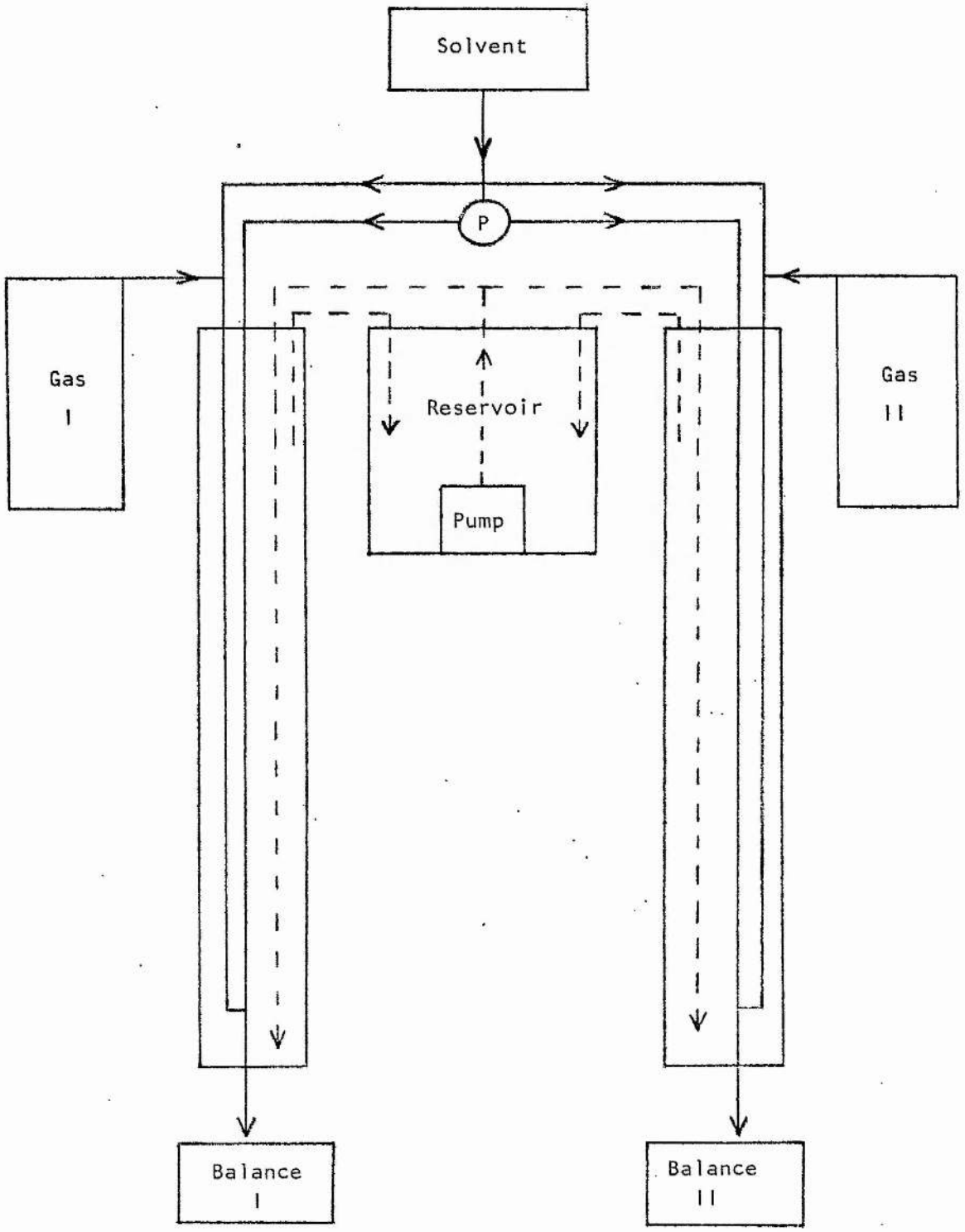


Figure 6 : ARRANGEMENT FOR DOUBLE SET OF ABSORPTION TUBES

on helium and hydrogen. (The gases should have solubilities which are not too different, so that about the same time is required for a measurement on each.) See also Appendix VI for a photograph.

The second set of absorption tubes was constructed with another modification which allows even better filling of the tubes after a run, and also prevents the scouring out of the graduations on the burette due to the constant flow of water in the thermostat. This is shown in Figure 7. The burette was mounted in the centre of a wider absorption tube (17 mm diameter), and left open at the top so that all the gas is displaced upwards at the end of a run, through tap M which is of course closed during the determination. The volume of gas within the measuring section can also be smaller with this arrangement, so that the effect of pressure fluctuations is minimised.

(d) Advantages of this technique

The method used is capable of measuring the solubility of gases in a large variety of liquids, over a wide temperature range, and around atmospheric pressure. It is a useful alternative to the batch method, and offers the following advantages:

(i) The apparatus can be constructed fairly easily and it is not expensive.

(ii) It can be operated without continuous supervision, requiring only the periodic recording of readings which are simple to make.

(iii) There is no possible supersaturation of solvent by gas, and fresh solvent is continuously being exposed.

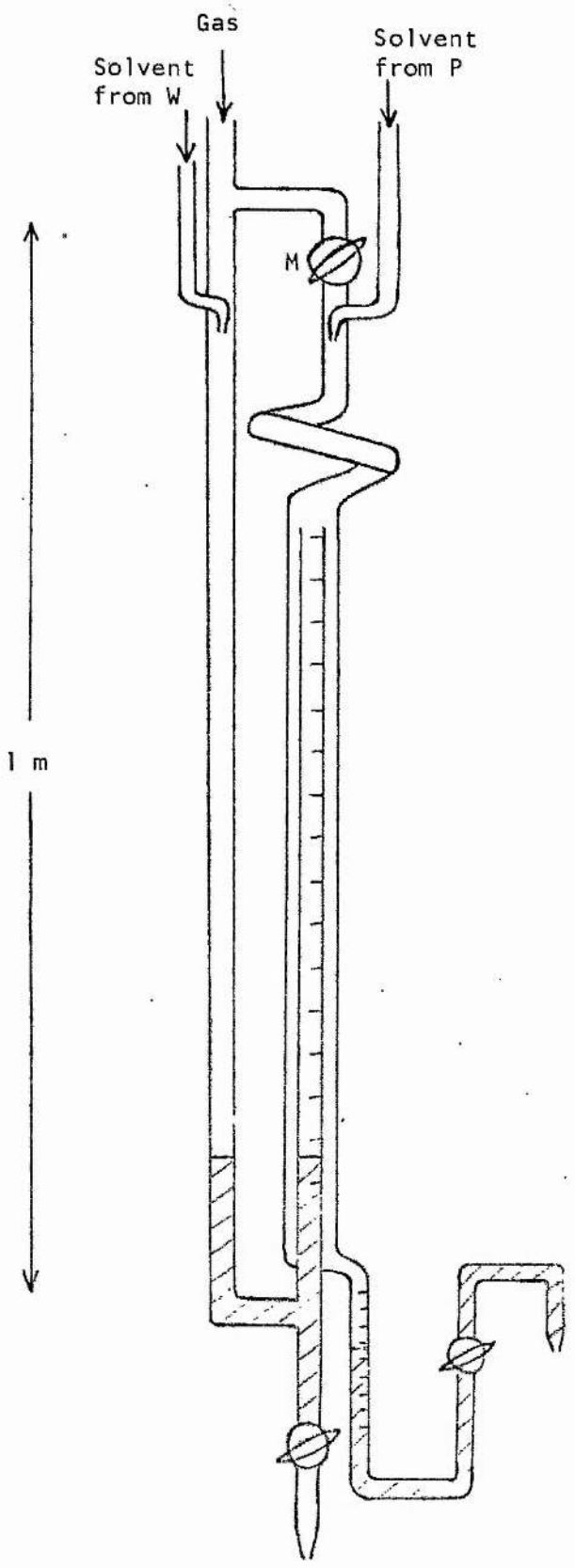


Figure 7 : CONCENTRIC ABSORPTION TUBE AND GAS BURETTE

(iv) Gas composition does not alter during a run since solvent vapour pressure is constant throughout, and there is no experimental difficulty in bringing gas and solvent together initially.

(v) The results are reproducible within 0.5%, and reliability increases with the number of readings taken and the time taken for a run. It has been pointed out[10] that the results seem to be about 1-2% lower than some others on the same systems. This might be due to incomplete rigour in degassing the solvent, and/or some very slow solubility of the last traces of gas. Nevertheless, the method of use of the results involves a calculation of differences between them, so that these small (consistent) errors for the most part will cancel out.

4. UNITS FOR SOLUBILITY MEASUREMENT

Many ways of expressing a solubility have been used in the literature. These are reviewed in references 3 and 40. Most of them are of historical origin and were most suited to the method of measurement used to obtain them. All are interconvertible, and related also to the more thermodynamically useful unit of mole fraction.

The unit of solubility used in this work is also empirical. It is given the symbol s, and is defined as the volume of gas in cm^3 (corrected to 273.1 K and 1 atmosphere = 101.3 kN m^{-2}) dissolved by 1 kg of solvent, under a gas pressure of 1 atmosphere.

i.e. if V cm^3 = volume of gas dissolved at pressure P and temperature T,

and m kg = corresponding mass of solvent,

then

$$s = \left(V \times \frac{273.1}{T} \times \frac{P}{760}\right) \frac{1}{m} \cdot \frac{760}{P} \text{ cm}^3 \text{ kg}^{-1}$$

$$= \frac{V}{m} \times \frac{273.1}{T} \text{ cm}^3 \text{ kg}^{-1}$$

This result is obtained for the gas at its partial pressure within the apparatus, which is the pressure of the atmosphere less the appropriate solvent vapour pressure. These factors vary from experiment to experiment. However, the result is always expressed for a partial gas pressure of one standard atmosphere by applying Henry's law: the volume of gas dissolved into a given mass of solvent is independent of its pressure.

Thus in the expression of a result, the gas is assumed to obey the ideal gas law, and Henry's law. In Appendix III it is shown that for the gases and conditions used, no significant error is introduced because of this.

CHAPTER 3 THEORETICAL ASPECTS OF SOLUBILITY

1. THERMODYNAMIC METHODS AND SYMBOLS

Thermodynamics deals with the average properties of a macro-system, and does not furnish details of its micro-structure. Nevertheless any acceptable theory of micro-structure must be consistent with the observed macroscopic properties examined by thermodynamic methods. In fact, for a satisfactory model of structure, statistical methods can be used to calculate thermodynamic functions.

In this chapter, the thermodynamic functions are derived for gas solubilities, and then current theories of structure in aqueous systems are outlined, with their relevance to thermodynamic parameters.

The following symbols are used in the rest of this thesis, with the significance shown.

ΔX = change in function X

X° = standard value of function X

$\bar{X}$ = partial molal value of function X

G = Gibb's free energy

H = enthalpy

S = entropy

C_p = heat capacity (at constant pressure)

μ = chemical potential

T = temperature

p = pressure

c = concentration

n = number of moles

x = mole fraction

s = solubility

m = mass

ρ = density

R = gas constant (= 8.314 J K^{-1} mol^{-1})

ℓn = natural logarithm

log = logarithm to base 10

2. THERMODYNAMIC FUNCTIONS

(a) Equilibrium of a gas with its solvent

The equilibrium studied exists between a gas phase and a solution phase. The solubility of the gaseous solute measures its partition between the two phases when equilibrium is reached. So, if the gas is A, the equilibrium reaction is represented by

$$A_{(g)} \rightleftharpoons A_{(soln)}$$

The position of this equilibrium is measured by its equilibrium constant (K) which can be related to the measured solubility as follows

$$K_a = \frac{\text{activity of solute A in solution phase}}{\text{activity of solute A in gas phase}}$$

∴ (i) if the gas is ideal, and forms an ideal solution,

$$K_x = \frac{\text{mole fraction of A in solution}}{\text{pressure of gas A}} = \frac{x_A}{p_A}$$

$$= \frac{n_A}{n_A + n_B + n_C} \cdot \frac{1}{p_A} \qquad \text{where B = water, C = alcohol}$$

$$\doteqdot \frac{n_A}{n_B + n_C} \cdot \frac{1}{p_A} \qquad \text{since } n_A \ll (n_B + n_C)$$

i.e. $K_x = \frac{s}{22{,}414} \cdot \frac{1}{n_B + n_C}$ atm^{-1} since p_A = 1 atm for definition of s.

Or (ii) if the gas is ideal, and forms an ideal dilute solution,

$$K_c = \frac{\text{concentration of A in solution}}{\text{pressure of gas A}} = \frac{c_A}{p_A}$$

$$= \frac{n_A}{p_A} \cdot \frac{1}{V} \quad \text{where V = volume of solution}$$

$$= \frac{n_A}{p_A} \cdot \frac{\rho}{m}$$

i.e. $K_c = \frac{s\rho}{22{,}414}$ atm^{-1} mol dm^{-3} since p_A = 1 atm, m = 1 kg for definition of s.

From equilibrium constants, standard thermodynamic functions may be obtained. First of all, however, it is implicit in the above alternatives that a clear decision must be made about standard reference states.

(b) Choice of standard state

For the gas phase (assuming ideal behaviour), the standard state is a partial pressure of one standard atmosphere (101.3 kN m^{-2}), which is also the standard to which is calculated the solubility unit, s.

For the solution phase, however, the standard state can be taken as

either (i) gas at a mole fraction of unity in the solution,

or (ii) gas at a concentration of 1 mol dm^{-3} in the solution.

Both of these standard states are unrealisable since, as shown in Appendix III, the concentration of gas in solution is always less than 0.05 mol dm^{-3}. To a great extent, therefore, the choice is arbitrary, and it does not affect the conclusions drawn from the data. Nevertheless it must be defined clearly, and it is felt that the standard based on mole fraction is more appropriate for this work, since

(i) mole fraction is more descriptive of relative abundances of molecules in the solution phase;

(ii) units of volume are excluded from the calculations;

(iii) it is consistent with the use of mole fraction to describe the composition of the aqueous alcohol solvent. The effects on water structure of both the gas and the alcohol are investigated, so these quantities are homogeneous.

Some workers in this field have adopted this standard state based on mole fraction, e.g. Smith *et al.*[10], Battino and Wilhelm[2], and Hildebrand[7] (who also uses a standard mole fraction of 10^{-5} for comparison of entropy changes during the solution of gases). Others have adopted the standard state based on concentration, e.g. Eley[66] and Ben Naim[16]. Comparison can be made between sets of results based on the two different standard states by means of the relationship between them, as calculated in Appendix IV.

(c) Formulation of thermodynamic functions

The changes in the partial molal free energy (or chemical potential), enthalpy, and entropy were calculated for the gas (A) as it moves from a hypothetical partial pressure of one atmosphere to a solution containing a hypothetical unit mole fraction of it,

i.e. $A_{(g)}$ (p = 1 atm.) $\longrightarrow$ $A_{(soln)}$ (x = 1).

In the calculations, the gas is assumed to be ideal, and also to obey the laws of ideal solutions. For a justification of this, see Appendix III.

The solvent is a mixture of components B (water) and C (alcohol), so we have for gas A:-

(i) $\mu_{(g)} = \mu^{\circ}_{(g)} + RT \ln p$ if A is ideal gas,

and $\mu_{(soln)} = \mu^{\circ}_{(soln)} + RT \ln x$ if solution of A is ideal.

At equilibrium, $\mu_{(g)} = \mu_{(soln)}$

$\therefore \quad \mu^{\circ}_{(soln)} - \mu^{\circ}_{(g)} = RT \ln p - RT \ln x$

i.e. $\Delta\mu^{\circ} = - RT \ln \frac{x}{p}$

i.e. $\Delta\bar{G}^{\circ} = - RT \ln \left(\frac{s}{22,414} \cdot \frac{1}{(n_B+n_C)}\right)$ as on P.33-34

$\therefore \quad \underline{\Delta\bar{G}^{\circ} = 2.303RT[4.350 + \log(n_B+n_C) - \log s]} \ldots\ldots\ldots (1)$

(ii) $\Delta\bar{H}^\circ = \Delta\bar{G}^\circ + T\Delta\bar{S}^\circ$

$= \Delta\bar{G}^\circ - T\frac{d\Delta\bar{G}^\circ}{dT}$

$\therefore \frac{\Delta\bar{H}^\circ}{T^2} = \frac{\Delta\bar{G}^\circ}{T^2} - \frac{1}{T}\frac{d\Delta\bar{G}^\circ}{dT}$

$= -\frac{d}{dT}\left(\frac{\Delta\bar{G}^\circ}{T}\right)$

$= -\frac{d(\frac{1}{T})}{dT} \cdot \frac{d}{d(\frac{1}{T})}\left(\frac{\Delta\bar{G}^\circ}{T}\right)$

$= \frac{1}{T^2}\frac{d}{d(\frac{1}{T})}\left(\frac{\Delta\bar{G}^\circ}{T}\right)$

i.e. $\Delta\bar{H}^\circ = -2.303R\frac{d}{d(\frac{1}{T})}\log s$ ..... (2)

(iii) $\Delta\bar{S}^\circ = \frac{\Delta\bar{H}^\circ - \Delta\bar{G}^\circ}{T}$ ..... (3)

(iv) $\Delta\bar{C}_p^\circ = \frac{d\,\Delta\bar{H}^\circ}{dT}$

i.e. $\Delta\bar{C}_p^\circ = \frac{\Delta\bar{H}_2^\circ - \Delta\bar{H}_1^\circ}{T_2 - T_1}$ ..... (4)

(d) Treatment of experimental results

For a gas in a given solvent, solubilities were usually measured at 7 temperatures in the range 4-61°C corresponding to the values of $\frac{1}{T} \times 10^4$ approximately equal to 36, 35, 34, 33, 32, 31, and 30. The function log s was plotted against $\frac{1}{T}$, and the best curve was drawn through the points : see Figure 8a.

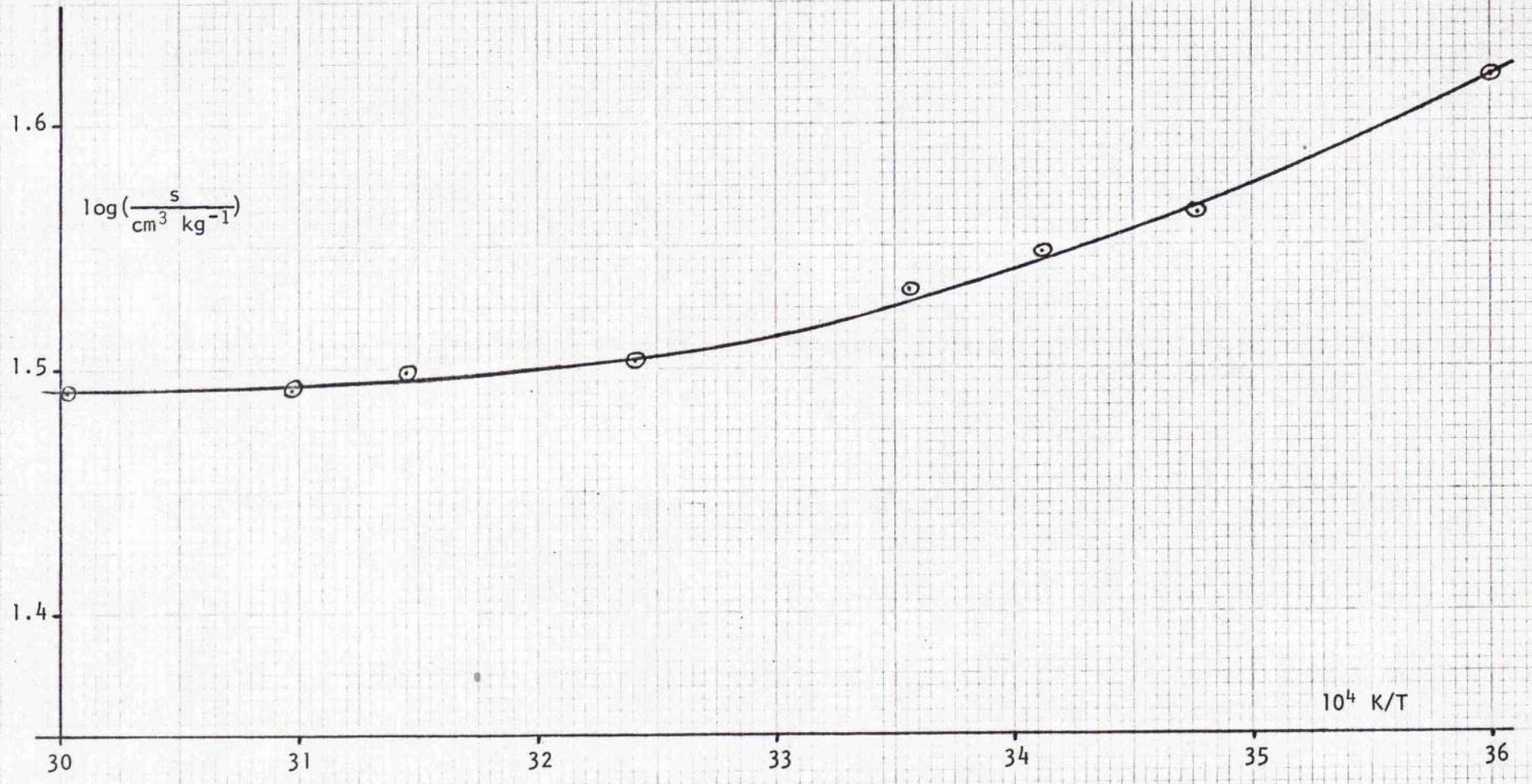


FIGURE 8a: Solubility curve for argon in aqueous ethanol of mole fraction 0.105

Now for these integral values of $\frac{1}{T} \times 10^4$,

(i) values of s can be interpolated and $\Delta\bar{G}°$ calculated by equation (1);

(ii) the slope of the tangent to the curve can be measured and $\Delta\bar{H}°$ calculated by equation (2);

(iii) $\Delta\bar{S}°$ is obtained from $\Delta\bar{G}°$ and $\Delta\bar{H}°$ by equation (3).

Then the several isotherms of these functions were plotted for a given aqueous alcohol system against the mole fraction of the alcohol (obtained for each mixture used by density calibration as on P.19).

Now it is essential that the experimental accuracy is high enough to warrant a treatment of this type. The accuracy is least for the lowest values of s, i.e. s = (10.0 $\pm$ 0.1) $cm^3\ kg^{-1}$, so that the possible error in s is 1%, and in log s it is 0.5%. (For s = 100, the error in log s is about 0.2%.) This error could persist in the solubility curve, but two independent checks are provided on the interpolated values of log s.

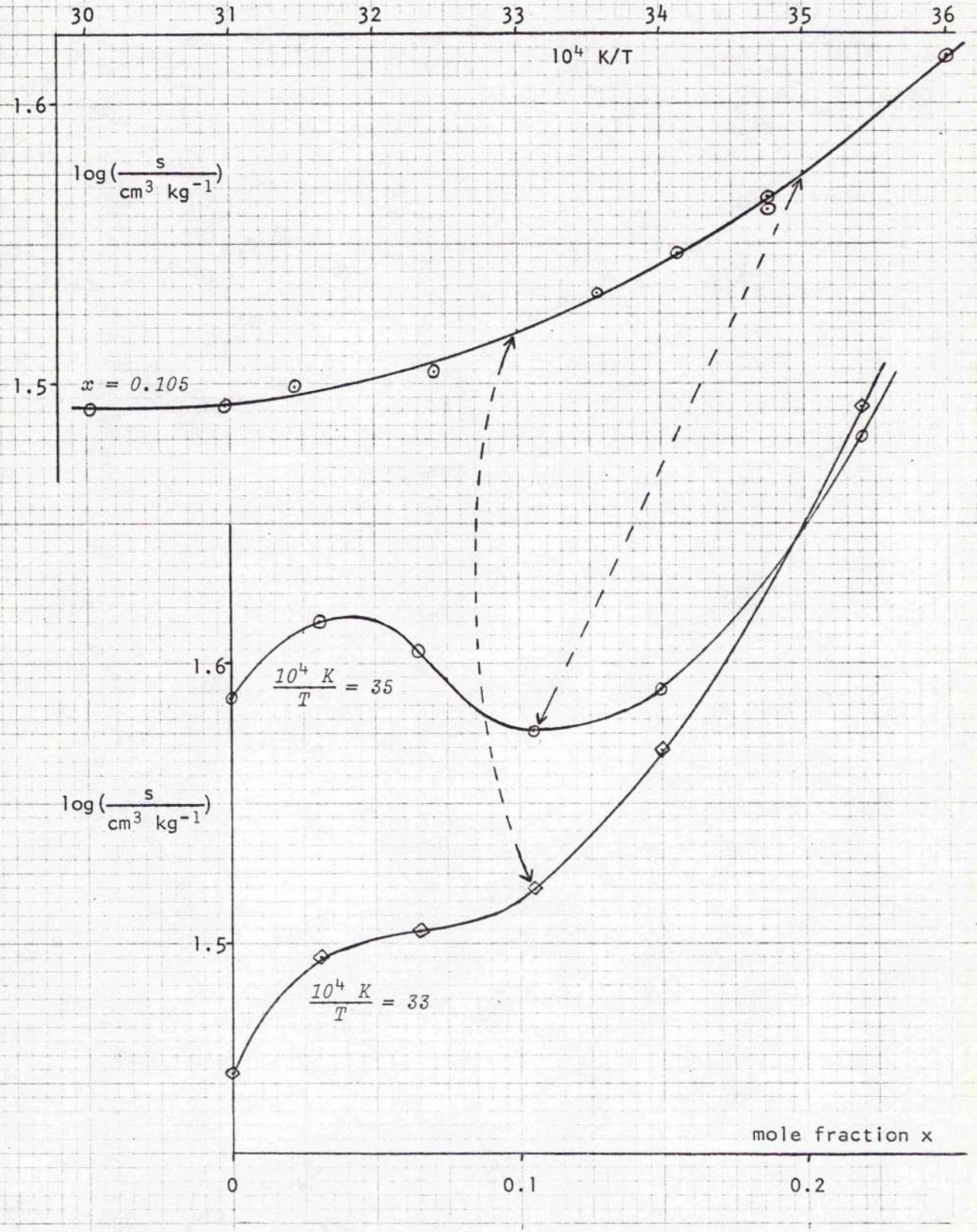
(i) Solubility isotherms are smoothed out over the different mole fractions of the alcohol to give values of log s consistent with the accuracy of the solubility curve. (See Figure 8b).

(ii) From equations (2) and (4) above,

$$\Delta\bar{H}° = -2.303R \frac{\Delta \log s}{\Delta(\frac{1}{T})}$$

and $$\frac{\Delta\bar{H}°_2 - \Delta\bar{H}°_1}{T_2 - T_1} = \Delta\bar{C}°_p \ ,$$

FIGURE 8b : Smoothing of solubility isotherms
(for argon in aqueous ethanol)



where $\Delta\bar{C}_p^\circ$ is assumed to change only slightly and slowly over the temperature range used, as has been found true in all the systems studied. Thus, a set of interpolated values of log s is estimated from a curve for the integral values of $\frac{1}{T} \times 10^4$. The difference between successive pairs of these is calculated, and this is proportional to $\Delta\bar{H}^\circ$. Then the difference between successive pairs of these differences is calculated, and this is approximately proportional to $\Delta\bar{C}_p^\circ$. If necessary, the original values of logs are then adjusted (within the limits of experimental errors) to give approximate constancy in this second difference. The following typical table of results shows the method. (For Ar in aqueous ethanol, x = 0.105; refer also to Figure 8)

$\frac{1}{T} \times 10^4$	log s	Δ log s	ΔΔ log s
36	1.618		
		42	
35	1.576		9
		33	
34	1.543		8
		25	
33	1.518		8
		17	
32	1.501		8
		9	
31	1.492		8
		1	
30	1.491		

It is found that ΔΔ log s is either constant or shows a slight decrease as temperature rises, so that considerable confidence may be placed in the solubility curve obtained.

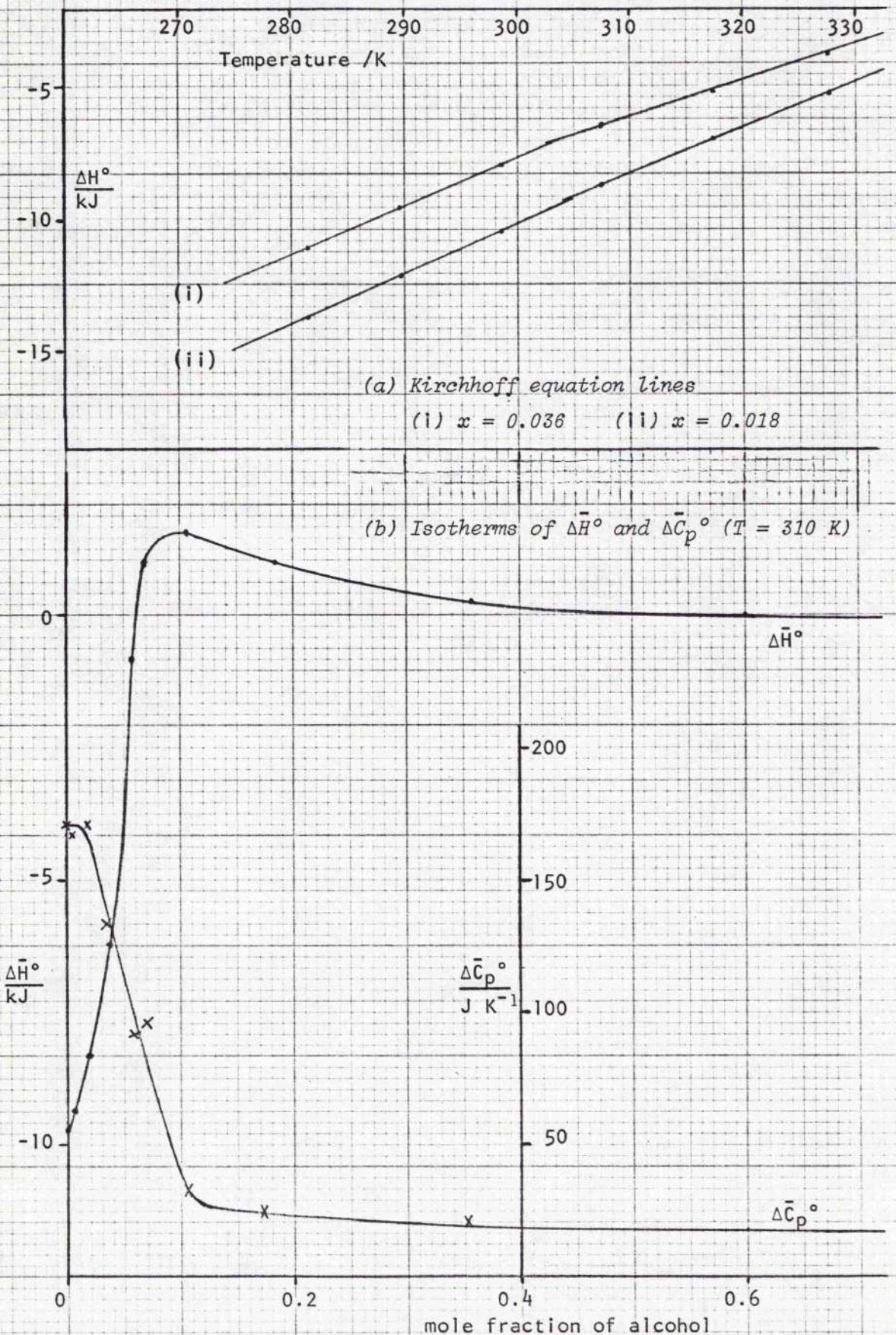
Now in order to obtain values for $\Delta\bar{H}°$, rather than draw tangents to the curves, it was found more convenient and accurate to use the method referred to above. Using the data in the first two columns of the above table for each solvent mixture in a given system, a computer was programmed to calculate each $\Delta\bar{H}° = \Delta \log s \times \frac{2.303R}{10^{-4}}$ (programme FINDH - Appendix V).

These $\Delta\bar{H}°$ values correspond to $\frac{1}{T}$ midway between the reference $\frac{1}{T} \times 10^4$, so they are graphed against temperature, the best line drawn through the points, and then the required values of $\Delta\bar{H}°$ for the reference temperatures can be interpolated: see Figure 9a.

The slope of this line is of course equal to $\Delta\bar{C}_p°$. Empirically it was found that the line usually has a slight curvature, but without error, it can be approximated to two straight lines as shown. This assumes that $\Delta\bar{C}_p°$ is constant over each temperature range 280-300 K, and 300-330 K. The possible error in $\Delta\bar{C}_p°$ is in fact very large, but it is used mainly as a check on the accuracy of $\Delta\bar{H}°$.

Values of $\Delta\bar{C}_p°$ for T = 280-300 K and 300-330 K, and interpolated values of $\Delta\bar{H}°$ for T = 290 K and 310 K are measured, and a further check on their validity is obtained by comparing them with those for other compositions of the solvent; i.e. $\Delta\bar{C}_p°$ and $\Delta\bar{H}°$ are plotted against mole fraction of the alcohol, and the curve is smoothed out as shown in Fig. 9b. From the curve the most probable values of $\Delta\bar{C}_p°$ and $\Delta\bar{H}°$ are selected for use

FIGURE 9 : Derivation and check of $\Delta\bar{H}°$ and $\Delta\bar{C}_p°$
(for argon in aqueous t-butanol)



in the equation

$$\Delta\bar{H}^\circ = \Delta\bar{H}^\circ_0 + \Delta\bar{C}^\circ_p(T - T_0),$$

which gives a fairly accurate algebraic interpolation of $\Delta\bar{H}^\circ$, well within its estimated error of about 2%.

From the experimental results, there is thus available for a set of temperatures T (corresponding to integral $\frac{1}{T} \times 10^4$) values of log s with a probable error of less than 0.5% and values of $\Delta\bar{H}^\circ$ with a probable error of less than 2%. So the probable error in $\Delta\bar{G}^\circ$ is less than 0.5%, and in $\Delta\bar{S}^\circ$ less than 2.5%, as calculated by equations (1), (2), and (3).

Based on these equations, a computer programme (DGHS21 - see Appendix V) was written to process the results, and also to carry out the algebraic interpolation for $\Delta\bar{H}^\circ$ referred to above. For a given system, the results are presented as one plane of a three-dimensional array, so that from its third dimension are obtained the calculated values of the parameters $\Delta\bar{G}^\circ$, $\Delta\bar{H}^\circ$, and $\Delta\bar{S}^\circ$, for each $\frac{1}{T}$ and each mole fraction of the alcohol in the solvent. Thus isotherms of these parameters can be studied as a function of the mole fraction of the alcohol. It is also possible to compare the changes in $\Delta\bar{C}^\circ_p$ for each system, although with much less precise quantitative significance.

3. STRUCTURAL THEORIES OF WATER

Some lively controversy still exists about the fundamental assumptions in the theories of water structure. One of the most recent reviews on this subject by Frank[67] attempts to show what water must be like, as

contrasted to what it might be like. At the same time, the reviewer freely admits the present unsettled state of the subject, and the difficulties associated with a complete solution to the problem.

This thesis is not concerned with a criticism of these theories, but it is relevant to notice how gas solubility data have featured in their developments. Also, in any satisfactory structural theory, thermodynamic parameters must be satisfied, and the following summary shows their influence on the problem.

(a) Historical development of a mixture model

One of the earliest models for water, due to Chadwell[68] (1927), treated the liquid as a mixture of monomers, dimers, and trimers of H_2O, whose concentrations varied with temperature. $(H_2O)_4$ and $(H_2O)_8$ were also proposed later[69] but evidence is lacking for any of these species.

Eley[66] in 1939 calculated the thermodynamic functions associated with the solution of the noble gases in water. He suggested that the enthalpy and entropy changes could be accounted for by describing the gas molecule entering a cavity which has been formed in the solvent. This cavity formation was the critical step in the process, having associated with it most of the enthalpy and entropy changes. At low temperature, cavities already exist in a structured form of the liquid.

Frank and Evans[70] in 1945 presented their paper in which the famous term "iceberg" was first used to describe the structured component of water. They postulated that a gas molecule built a microscopic iceberg around it, whose size was related to the size of the gas

molecule. The term "iceberg" was not necessarily to mean exactly icelike, but rather a region of water molecules which had quasi-crystallinity. Also, by invoking Le Chatelier's principle, they suggested that foreign molecules would stabilise the icebergs where more space exists for them, and so increase their quantity; i.e. that the equilibrium in water between open and close-packed structures was shifted in the direction of the open form.

The thermodynamic implications of this lie in the directions of $\Delta\bar{H}°$ and $\Delta\bar{S}°$, which are both negative. The gases are very insoluble, i.e. $\Delta\bar{G}°$ is positive. The process is thus favourable in terms of enthalpy loss, but unfavourable in terms of entropy loss, so that the solubility of gases is entropy controlled (first proposed by Butler[71] for alcohols in water). This is in accord with the picture that when icebergs form round a gas molecule, bonds are made and disorder decreases. Attention is also drawn to the high heat capacity of water. This too is explained by the energy used to melt the icebergs as the temperature is raised. Further, for the solubility of gases, $\Delta\bar{C}_p°$ is positive, confirming the idea of increased order due to the solute, although Ben Naim[72] has criticised the simplicity of this explanation.

The nature of the icebergs was further discussed by Frank and Wen[73] in 1957, who used the term "flickering clusters" to indicate a co-operative process of hydrogen-bond making and breaking throughout the liquid. The statistical degree of "icelikeness" is proportional to the average size and half life of the clusters. Non-polar solute molecules provide barriers to the disruptive influences within the liquid since they cannot transmit the electrostatic forces associated with hydrogen-bond breaking.

In 1960, from the analogy of the structure of gas hydrates, Pauling[74] suggested that "loose" water molecules could be accommodated within the icebergs. This interstitial model was used by Frank and Quist[75] to calculate pressure-volume-temperature correlations for water. It did not give a good explanation for the thermodynamics of the solution of non-polar substances, however, and it has largely been abandoned. On the other hand, Wada,[76] at about the same time, used the original two state model with the minimum assumptions to calculate reasonable values for some physical properties of water.

Némethy and Scheraga[38a] formulated a mechanism of cluster formation based upon statistical methods to obtain partition functions. In a second paper[38b] they used this model to calculate the thermodynamic functions for aqueous solutions of hydrocarbons, and obtained very good agreement with experimental data. They showed that there was a higher probability of finding an iceberg near a solute molecule, due to the solute-solvent interactions affecting the energy levels of the water; i.e.

(i) in icebergs, H_2O energy levels are lowered because of an added van der Waals interaction with the solute molecules now present;

(ii) the energy levels of unbonded H_2O molecules are raised, because a strong water-water dipole interaction is replaced by weaker London forces; therefore more water molecules exist in the cluster form and fewer are unbonded, i.e. there is a nett increase in icelikeness.

Ben Naim[23] after work on gas solubilities, also suggested a similar mechanism for this model, based on distribution function equations. Added non-electrolyte lowers the chemical potential of the clusters more than the monomeric water, due to the inactivity of the solute molecule, so that the equilibrium within the water is shifted in favour of the more structured form.

Finally, in 1968, Frank and Franks[77] showed how the original theory could be used to explain the solubility of hydrocarbons in water by representing the solute as distributed between two phases - a quasi-clathrate solution in the icebergs, and a quasi-lattice (or regular) solution in the denser phase.

(b) Current aspects of the mixture model

In the development and discussions of this theory, the term "iceberg" or "icelikeness" has been frequently criticised (for example, see comments by Everett[78] and by Eley[78]) for implying a restrictive meaning to the hydrogen-bonded clusters of water. "Clathrate" or "cage structures" have been proposed as alternatives, but again these may carry undesirable connotations.

This mixture model is therefore best described as an equilibrium of two kinds of water:

(i) hydrogen-bonded molecules, with an open structure and a lower density; and

(ii) monomeric non hydrogen-bonded molecules, more closely packed and having a higher density;

i.e. $(H_2O)_n \rightleftharpoons nH_2O$.

The equilibrium is shifted to the left (in favour of more hydrogen-bonding) by the addition of non-electrolyte molecules. The position of the equilibrium also depends on the temperature, and the following estimates of size and population have been made:

Temperature °C	Average cluster size	Mole fraction of H-bonded mols	Authors
0	91	0.76	Némethy and Scheraga[38a]
70	25	0.61	
0		0.42	Wada[75]
100		0.2	
20	20		
6		0.73	Buijs and Choppin[79]
72		0.60	

The first two estimates are derived from theory, but the last authors base their estimate on the temperature dependence of the infra-red spectrum of water.

The mixture model is consistent with the directions and orders of magnitude of $\Delta\bar{H}°$, $\Delta\bar{S}°$, and $\Delta\bar{C}_p°$ for solubility of gases in water. Detailed calculations are unavailable to check these, however, since the partition functions for the model are too complicated to handle even with extensive computer operations.

Most of the workers who have been responsible for the recent development of the theory have also shown its implications in the concept of "hydrophobic bonding" (see references 23, 24, 37, 38 and 77). The interaction with water of simple non-polar solutes provided a model for such interaction of non-polar side chains in protein molecules, where the hydrophobic bond between these is thought to be responsible for their native configurations.

(c) An alternative continuum model

A challenge to the mixture model has been presented by a continuum model, based on the distortion rather than the rupture of hydrogen-bonds. In this model water has only one structure, and its thermodynamic properties are described by varying degrees of distortion of a completely hydrogen-bonded structure. The idea originated with Bernal and Fowler[80] in 1933, was developed in detail by Pople[81] in 1951, and further discussed by Bernal[82] in the Bakerian lecture in 1964. Eisenberg and Kauzmann,[83] in their textbook on water structure, indicate that mixture models are not in accord with some experimental data, especially from spectroscopy, and they favour the Pople model. With respect to gas solubilities, it has been used by Smith *et al.*[10], and by Hildebrand and Miller[84] to explain their experimental results.

It is not possible at this stage to state which of the two types of model is the better. In fact both seem to be valuable, even if for different purposes. Frank, in the latest review referred to,[67] considers Hildebrand's conclusions unacceptable, and remains convinced that a mixture model is necessary to explain especially solubility phenomena.

In the results of this work, attention is focussed on the manner in which the organic component of the solvent alters the values of $\Delta\bar{H}°$, $\Delta\bar{S}°$, and $\Delta\bar{C}_p°$ for the different gases. A comparison is also made of the magnitudes of these parameters for each of the five gases used. Where possible, some correlation is sought with the mixture model.

CHAPTER 4 RESULTS OF THE PRESENT INVESTIGATION

In this chapter, experimental results are tabulated in the form in which they were obtained. Solubilities of the several gases in the different solvents are given by s, the units of which (see P.31) are $cm^3\ kg^{-1}$. In every case the measurement is quoted as log s for a given temperature (t/°C) whose reciprocal on the Kelvin scale ($\frac{1}{T} \times 10^4$ K) is also given for reference. The solubility curves for each system are then drawn, $\log(s/cm^3\ kg^{-1})$ vs. 10^4 K/T, according to the method described on P.41.

A few of the results quoted were not actually determined by the author, but by T.J. Morrison or other co-workers, and full acknowledgment is made in the text where this is so;

i.e. (a) the solubilities of the gases in water for temperatures above 10°C, as published in references 8 and 12;

(b) the solubilities of argon and of carbon dioxide in the aqueous ethanol system;

and (c) some of the solubilities of carbon dioxide in the aqueous t-butanol system.

All the results are collected in this thesis, however, for use in the calculations, so that the survey and the comparisons can be as comprehensive as possible.

1. SOLUBILITIES OF HELIUM

(a) In Water

(i) *Author's results*

t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
5.2	35.93	0.970
10.9	35.21	0.961
21.3	33.97	0.930
59.2	30.09	0.953

(ii) *From Morrison and Johnstone*[8]

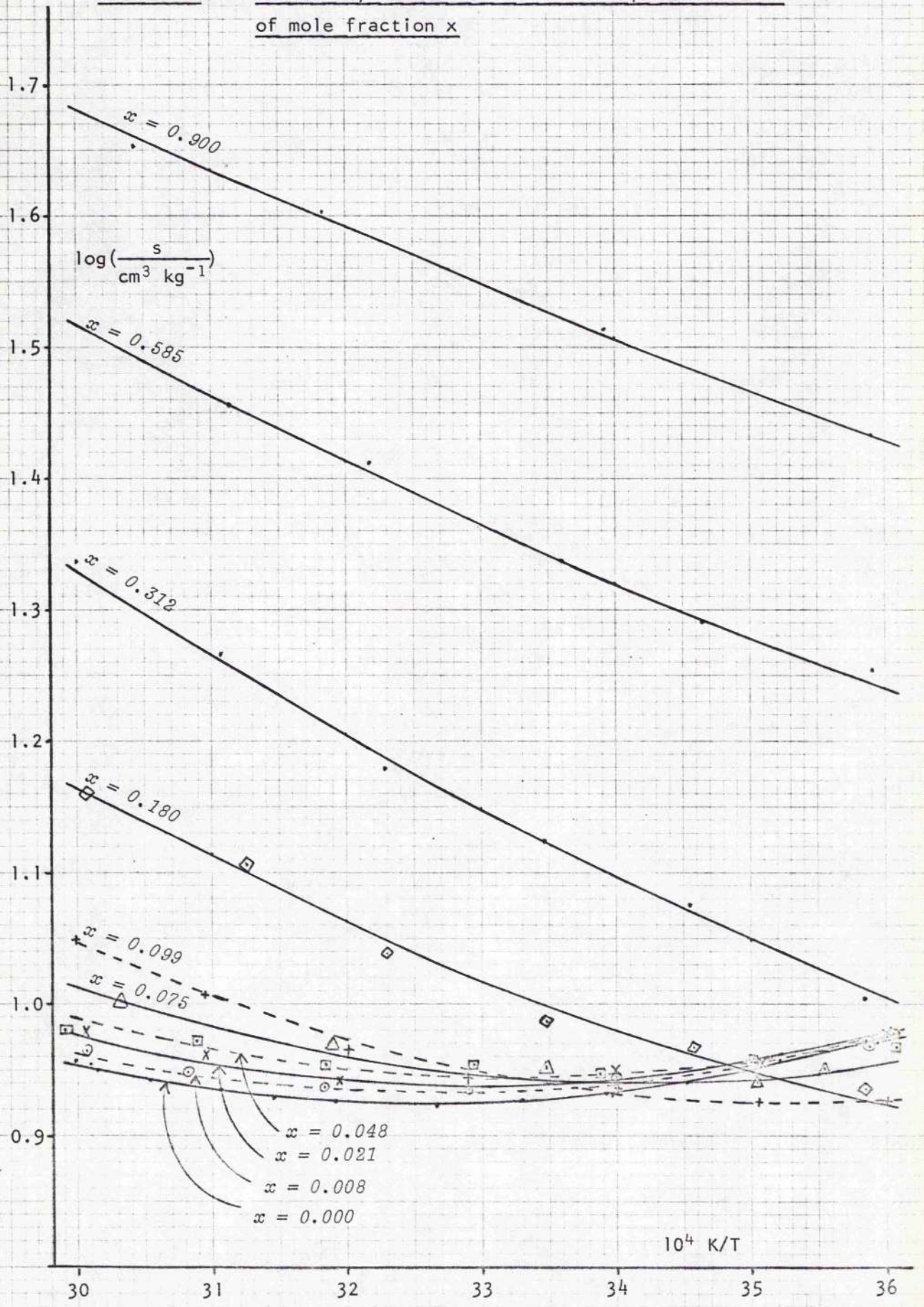
t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
4.6	36.01	0.975
6.0	35.83	0.971
11.0	35.20	0.956
13.2	34.93	0.948
16.6	34.51	0.940
21.7	33.92	0.931
27.4	33.28	0.927
33.0	32.67	0.921
40.4	31.90	0.925
44.9	31.45	0.927
48.9	31.06	0.934
54.4	30.53	0.940
58.6	30.15	0.949
60.5	29.98	0.955

(b) In aqueous ethanol, for the following mole fractions (x) of ethanol : see also Figure 10.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.2	36.06	0.976
	5.6	35.88	0.968
	12.3	35.04	0.954
0.008	21.0	34.00	0.945
	30.8	32.90	0.936
	41.1	31.83	0.937
	51.4	30.81	0.959
	59.6	30.06	0.964
(3)	4.2	36.06	0.967
	12.6	35.01	0.958
	22.2	33.87	0.947
0.048	30.6	32.93	0.953
	41.1	31.83	0.952
	50.7	30.88	0.971
	61.3	29.90	0.980
(5)	4.7	36.00	0.927
	12.2	35.05	0.926
	21.0	34.00	0.936
0.099	30.9	32.89	0.945
	39.4	32.00	0.963
	50.4	30.94	1.006
	60.3	29.99	1.049
(7)	5.9	35.84	1.003
	16.3	34.55	1.075
	25.6	33.48	1.123
0.312	36.6	32.29	1.176
	48.7	31.07	1.266
	60.2	30.00	1.336
(9)	5.4	35.90	1.432
	21.7	33.92	1.513
0.900	41.1	31.83	1.602
	55.6	30.42	1.652

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)	4.7	36.00	0.978
	12.1	35.07	0.954
	21.1	33.99	0.950
0.021	40.0	31.94	0.941
	49.8	30.95	0.961
	59.5	30.07	0.979
(4)			
	8.4	35.53	0.951
	12.3	35.04	0.940
0.075	25.6	33.48	0.952
	40.5	31.89	0.969
	56.7	30.31	1.001
(6)	5.9	35.84	0.936
	16.1	34.58	0.967
	25.7	33.47	0.986
0.180	36.6	32.29	1.039
	48.0	31.24	1.105
	59.7	30.05	1.160
(8)			
	5.4	35.90	1.254
	15.6	34.64	1.290
0.585	24.5	33.60	1.337
	37.7	32.18	1.411
	48.1	31.13	1.455

FIGURE 10 : Solubility curves for helium in aqueous ethanol of mole fraction x

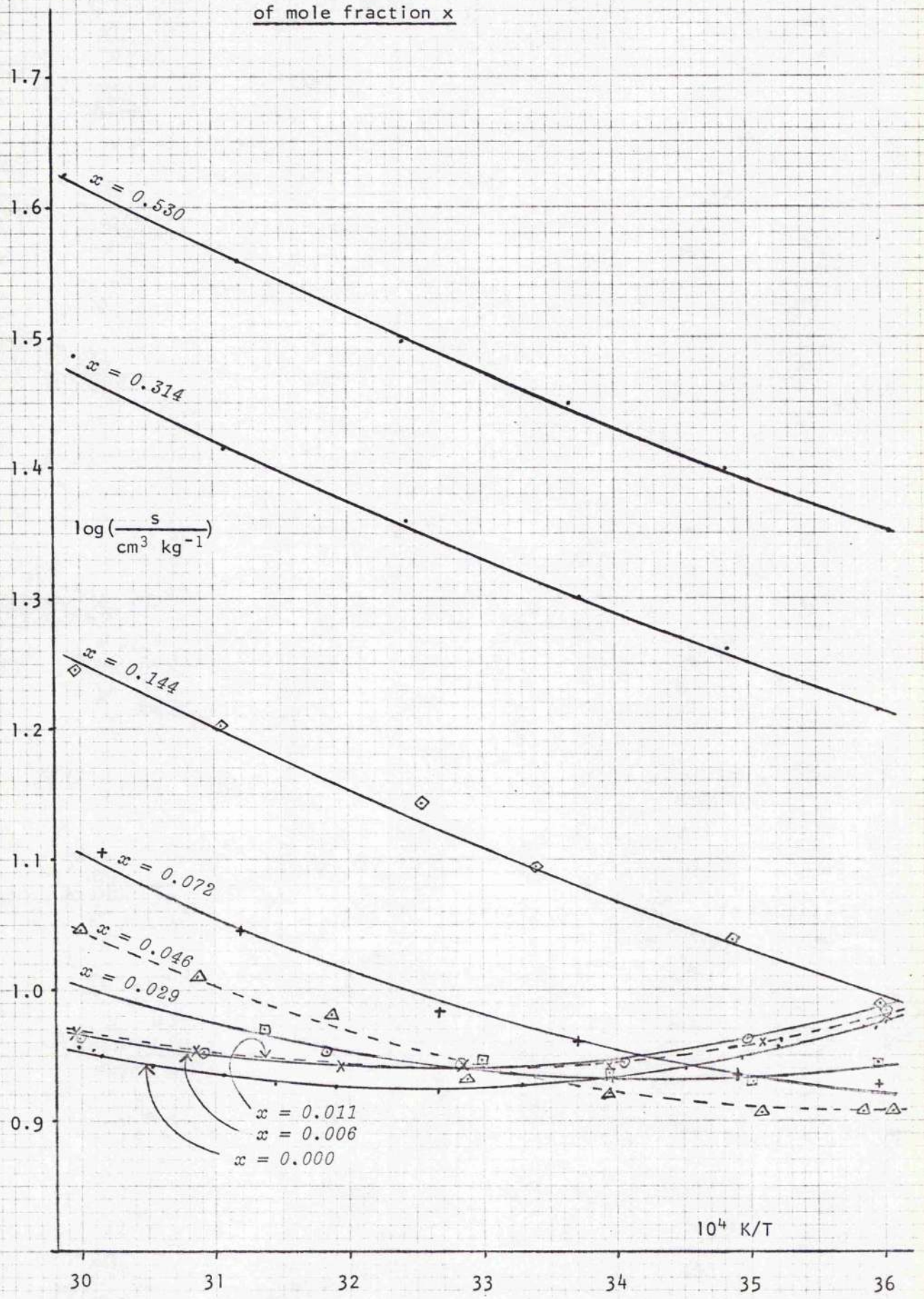


(c) In aqueous t-butanol, for the following mole fractions (x) of t-butanol : see also Figure 11.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.6	36.01	0.984
	12.9	34.97	0.962
	20.6	34.05	0.946
0.006	31.6	32.82	0.944
	41.2	31.82	0.952
	50.4	30.91	0.952
	60.3	29.99	0.963
(3)	5.1	35.94	0.944
	12.6	35.01	0.930
0.029	21.7	33.92	0.933
	30.0	32.99	0.946
	45.8	31.36	0.970
(5)	5.0	35.96	0.928
	13.5	34.90	0.933
0.072	23.6	33.70	0.960
	32.9	32.68	0.984
	47.5	31.19	1.045
	58.5	30.16	1.106
(7)	4.9	35.97	1.215
	14.1	34.82	1.261
0.314	23.4	33.72	1.300
	35.2	32.44	1.359
	48.6	31.08	1.413
	60.7	29.96	1.485

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)	4.7	36.00	0.979
	12.0	35.08	0.960
	21.6	33.93	0.942
0.011	31.5	32.83	0.942
	40.0	31.94	0.941
	50.9	30.86	0.954
	60.7	29.97	0.967
(4)	4.3	36.05	0.907
	6.0	35.83	0.907
0.046	12.0	35.08	0.906
	21.7	33.92	0.921
	31.0	32.88	0.931
	40.7	31.87	0.981
	50.9	30.86	1.009
	60.2	30.00	1.047
(6)	4.8	35.98	0.987
	13.7	34.87	1.039
0.144	26.3	33.40	1.094
	34.3	32.53	1.142
	48.9	31.06	1.201
	60.7	29.96	1.245
(8)	4.3	36.05	1.351
	14.1	34.82	1.399
0.530	24.0	33.66	1.449
	35.5	32.41	1.497
	47.5	31.19	1.559
	61.4	29.90	1.623

FIGURE 11 : Solubility curves for helium in aqueous t-butanol of mole fraction x



2. SOLUBILITIES OF HYDROGEN

(a) In Water

(i) *Author's results*

t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
4.6	36.01	1.319
5.2	35.93	1.320
10.9	35.21	1.289
21.3	33.97	1.257
23.8	33.68	1.251
32.1	32.77	1.233
59.2	30.09	1.212

(ii) *From Morrison and Billett*[12]

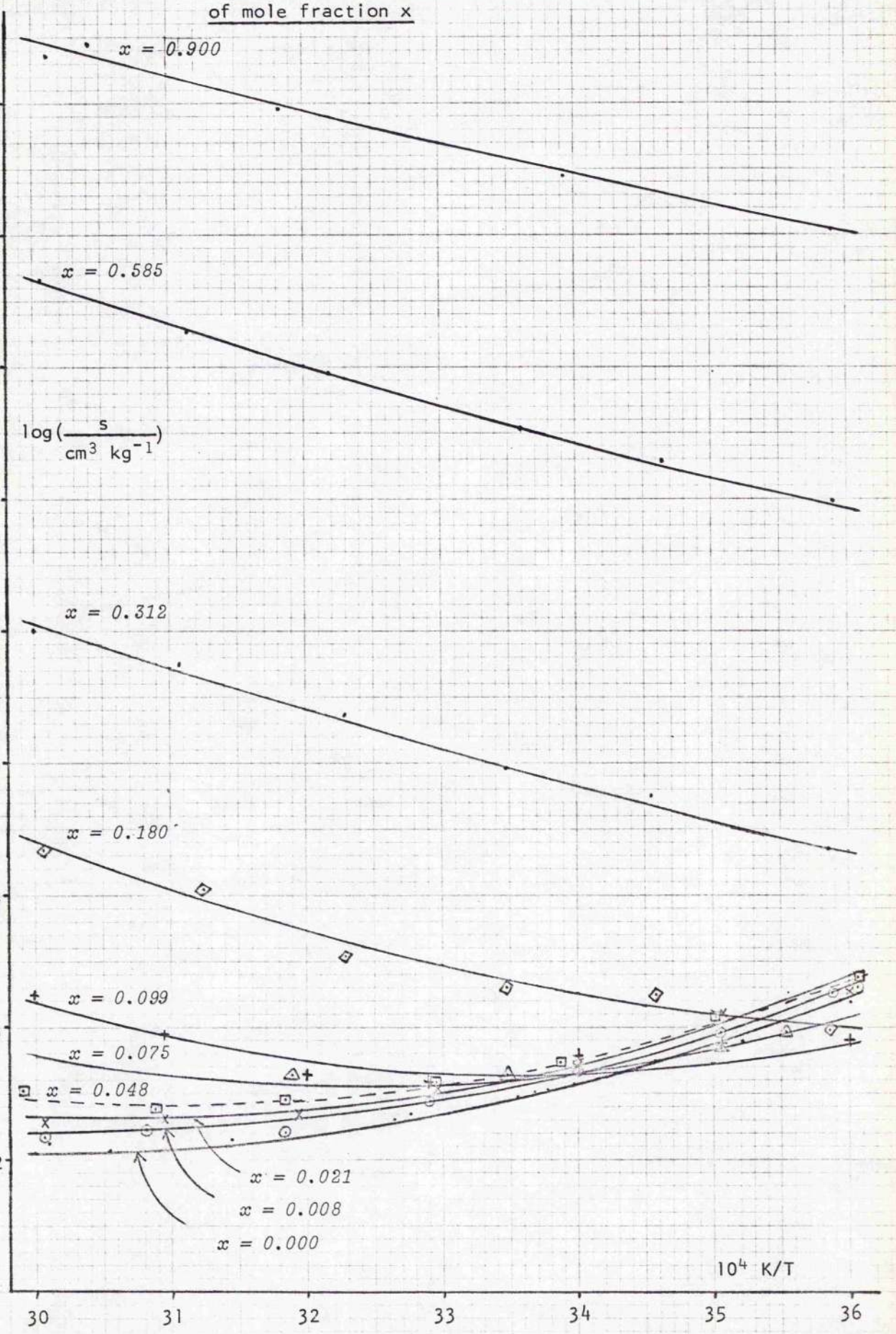
t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
12.3	35.04	1.284
16.1	34.58	1.272
23.0	33.77	1.252
25.0	33.55	1.248
33.2	32.63	1.230
45.0	31.44	1.214
54.4	30.53	1.206
60.3	29.99	1.206
65.5	29.54	1.208

(b) In aqueous ethanol, for the following mole fractions (x) of ethanol : see also Figure 12.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.2	36.06	1.330
	5.6	35.88	1.326
	12.3	35.04	1.295
0.008	21.0	34.00	1.267
	30.8	32.90	1.244
	41.1	31.83	1.220
	51.4	30.81	1.222
	59.6	30.06	1.218
(3)	4.2	36.06	1.338
	12.6	35.01	1.307
	22.2	33.87	1.272
0.048	30.6	32.93	1.257
	41.1	31.83	1.245
	50.7	30.88	1.238
	61.3	29.90	1.251
(5)	4.7	36.00	1.290
	12.2	35.05	1.278
	21.0	34.00	1.278
0.099	30.9	32.89	1.259
	39.4	32.00	1.264
	50.4	30.94	1.296
	60.3	29.99	1.325
(7)	5.9	35.84	1.433
	16.3	34.55	1.475
0.312	25.6	33.48	1.496
	36.6	32.29	1.536
	48.7	31.07	1.573
	60.2	30.00	1.600
(9)	5.4	35.90	1.904
	21.7	33.92	1.944
0.900	41.1	31.83	1.996
	55.6	30.42	2.046
	59.0	30.11	2.036

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)			
	4.7	36.00	1.327
	12.1	35.07	1.312
0.021	21.1	33.99	1.269
	30.3	32.96	1.253
	40.0	31.94	1.232
	49.8	30.95	1.231
	59.5	30.07	1.228
(4)			
	8.4	35.53	1.296
	12.3	35.04	1.286
0.075	25.6	33.48	1.262
	40.5	31.89	1.264
(6)	5.9	35.84	1.296
	16.1	34.58	1.325
	25.7	33.47	1.330
0.180	36.6	32.29	1.354
	48.0	31.24	1.403
	59.7	30.05	1.433
(8)	5.4	35.90	1.699
	15.6	34.64	1.729
0.585	24.5	33.60	1.753
	37.7	32.18	1.795
	48.1	31.13	1.827
	59.7	30.05	1.865

FIGURE 12 : Solubility curves for hydrogen in aqueous ethanol of mole fraction x

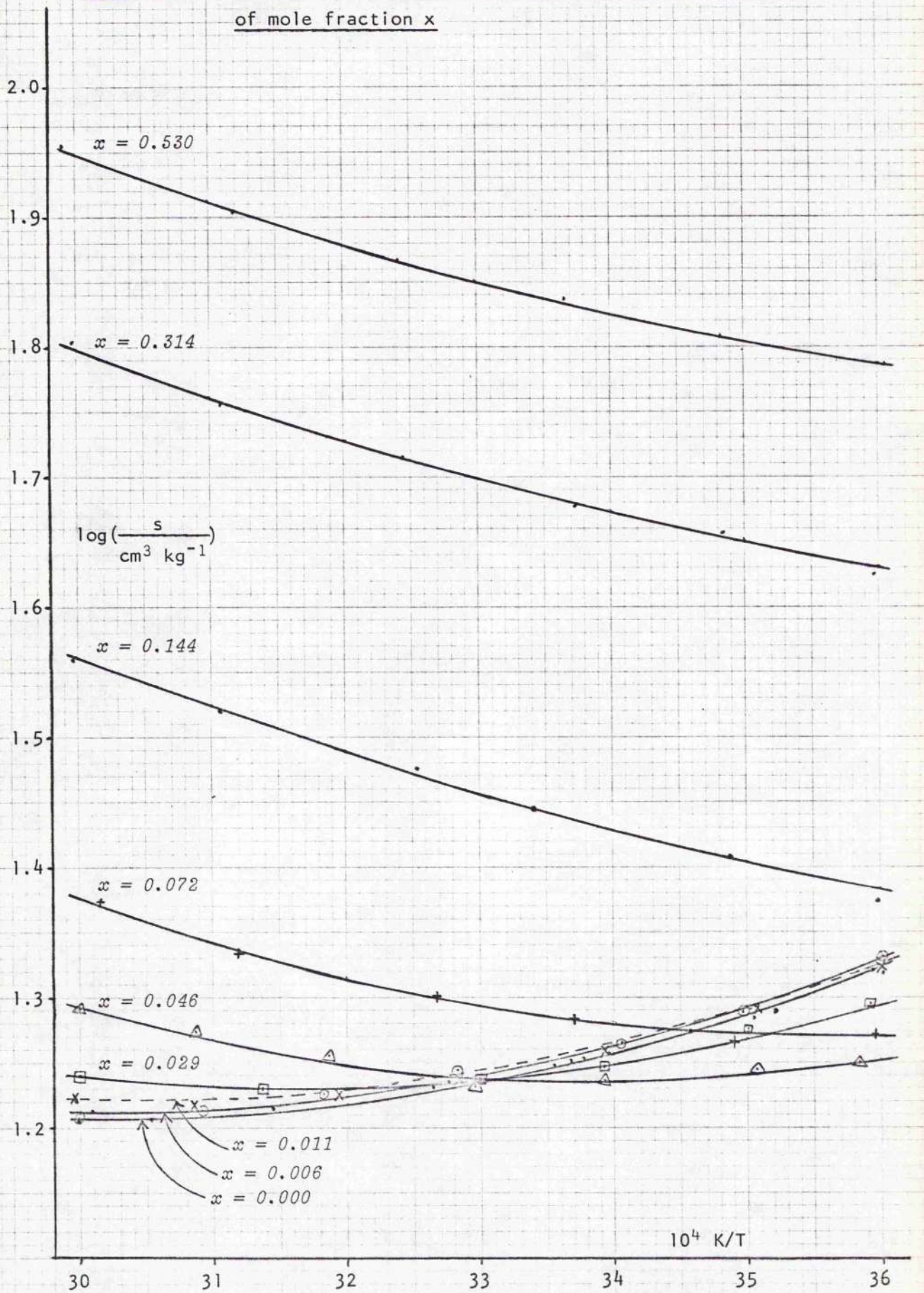


(c) In aqueous t-butanol, for the following mole fractions (x) of t-butanol : see also Figure 13.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.6	36.01	1.331
	12.9	34.97	1.288
	20.6	34.05	1.265
0.006	31.6	32.82	1.243
	41.2	31.82	1.227
	50.4	30.91	1.212
	60.3	29.99	1.208
(3)	5.1	35.94	1.291
	12.6	35.01	1.275
	21.7	33.92	1.246
0.029	30.0	32.99	1.236
	45.8	31.36	1.229
	60.2	30.00	1.240
(5)	5.0	35.96	1.271
	13.5	34.90	1.265
0.072	23.6	33.70	1.282
	32.9	32.68	1.301
	47.5	31.19	1.333
	58.5	30.16	1.374
(7)	4.9	35.97	1.625
	14.1	34.82	1.657
0.314	23.4	33.72	1.677
	35.2	32.44	1.715
	48.6	31.08	1.755
	60.7	29.96	1.803

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)	4.7	36.00	1.323
	12.0	35.08	1.291
	21.6	33.93	1.259
0.011	31.5	32.83	1.236
	40.0	31.94	1.226
	50.9	30.86	1.218
	60.7	29.97	1.223
(4)	6.0	35.83	1.250
	12.0	35.08	1.244
	21.7	33.92	1.236
0.046	30.5	32.96	1.231
	40.7	31.87	1.256
	50.9	30.86	1.273
	60.2	30.00	1.290
(6)	4.8	35.98	1.373
	13.7	34.87	1.408
0.144	26.3	33.40	1.444
	34.3	32.53	1.475
	48.9	31.06	1.520
	60.7	29.96	1.559
(8)	4.3	36.05	1.786
	14.1	34.82	1.808
0.530	24.0	33.66	1.836
	35.5	32.41	1.867
	47.5	31.19	1.903
	61.4	29.90	1.954

FIGURE 13 : Solubility curves for hydrogen in aqueous t-butanol of mole fraction x



3. SOLUBILITIES OF ARGON

(a) In Water

(i) *Author's results*

t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
4.6	36.01	1.670
6.4	35.77	1.645
25.4	33.50	1.484

(ii) *From Morrison and Johnstone*[8]

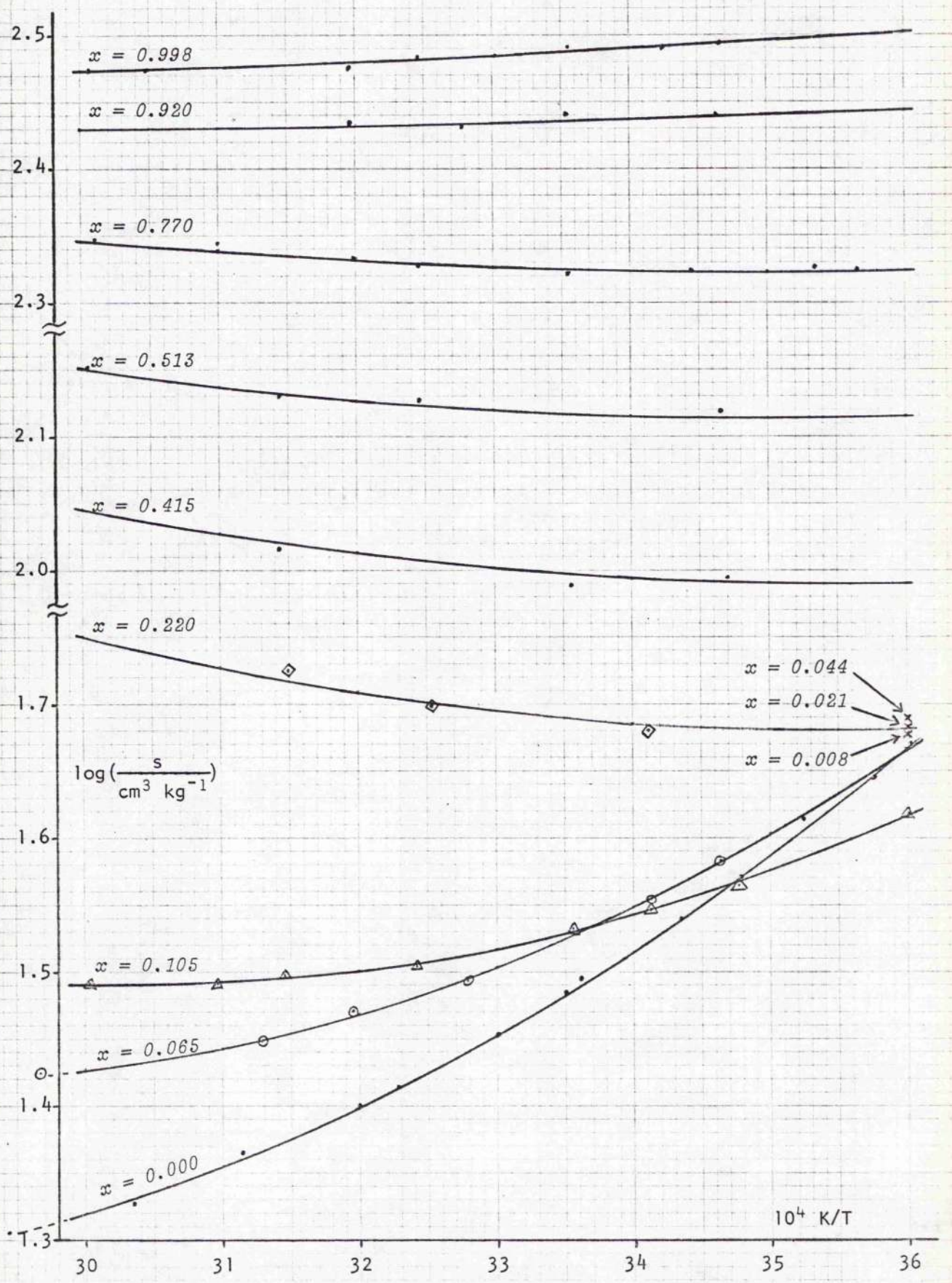
t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
10.7	35.24	1.612
14.3	34.79	1.570
18.2	34.33	1.539
24.4	33.61	1.493
29.8	33.01	1.452
36.6	32.28	1.413
39.4	32.00	1.400
47.8	31.14	1.364
56.3	30.36	1.328
66.3	29.46	1.306

(b) In aqueous ethanol, for the following mole fractions (x) of ethanol : *unpublished results of T.J. Morrison* : see also Figure 14.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1) 0.008	4.7	36.00	1.679
(2) 0.021	4.7	36.00	1.683
(3) 0.044	4.7	36.00	1.690
(4)	15.7	34.62	1.582
	19.9	34.12	1.554
0.065	31.9	32.79	1.494
	39.9	31.96	1.471
	46.5	31.29	1.449
	63.8	29.68	1.423
(6)	20.2	34.10	1.681
0.220	34.4	32.52	1.699
	44.5	31.49	1.725
(8)	15.5	34.65	2.119
0.513	35.0	32.45	2.127
	45.0	31.44	2.130
	59.9	30.03	2.151
(10)	7.4	35.65	2.325
	9.9	35.34	2.326
	17.2	34.45	2.322
0.770	25.1	33.54	2.321
	35.0	32.45	2.328
	39.5	31.99	2.332
	49.4	31.00	2.343
	59.1	30.10	2.348

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(5)	4.7	36.00	1.619
	14.5	34.77	1.563
0.105	20.0	34.12	1.547
	24.9	33.56	1.532
	35.4	32.41	1.503
	44.9	31.45	1.498
	49.7	30.97	1.491
	59.9	30.03	1.491
(7)	15.1	34.70	1.994
0.415	24.8	33.57	1.988
	45.0	31.44	2.017
(9)	15.7	34.62	2.440
0.920	25.1	33.54	2.440
	32.0	32.79	2.431
	39.6	31.97	2.435
(11)	15.5	34.65	2.495
	19.9	34.25	2.491
	25.1	33.54	2.491
0.998	29.9	33.01	2.484
	35.0	32.46	2.482
	39.8	31.96	2.476
	54.9	30.49	2.474
	59.6	30.06	2.473

FIGURE 14 : Solubility curves for argon in aqueous ethanol of mole fraction x

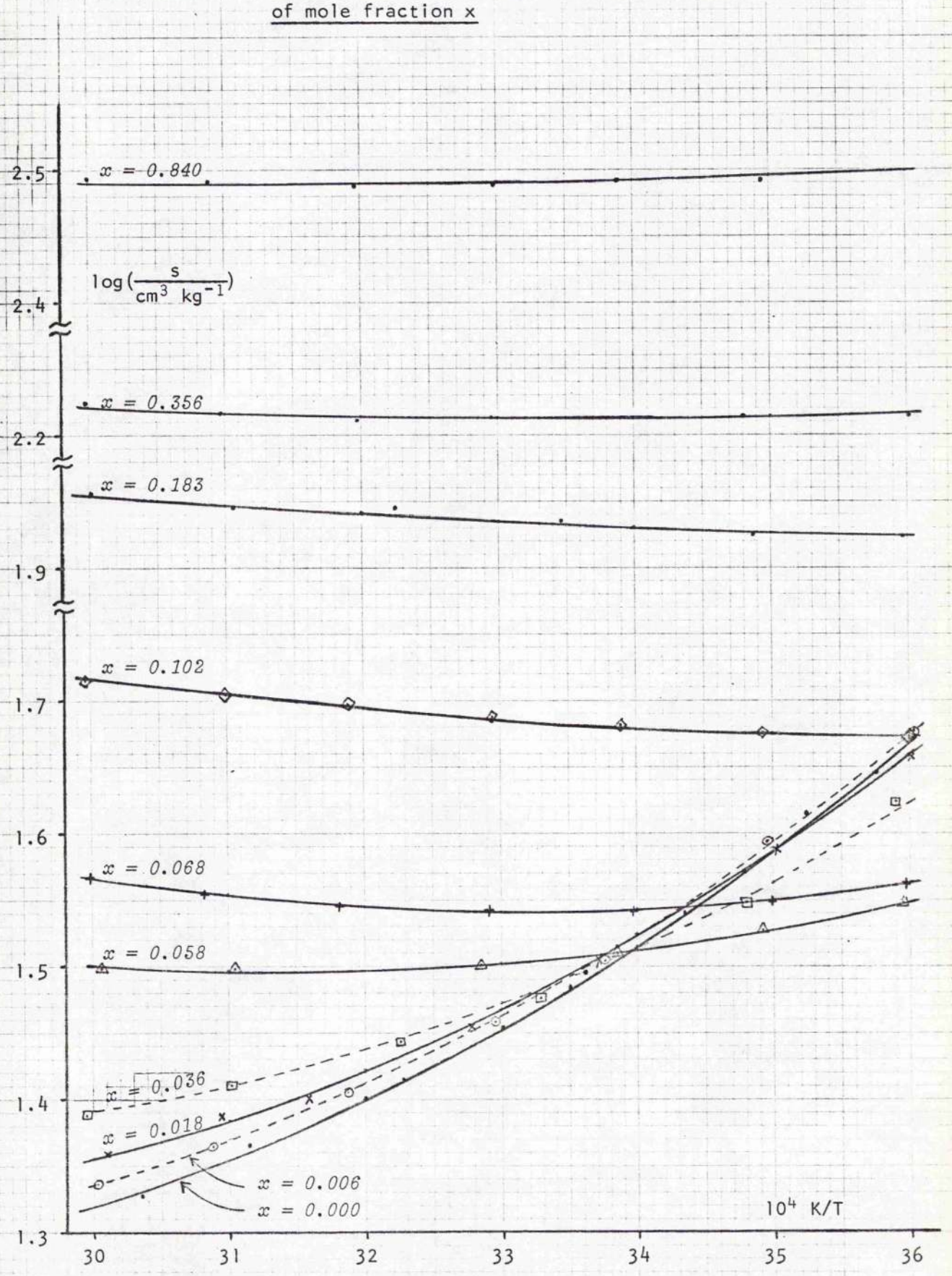


(c) In aqueous t-butanol, for the following mole fractions (x) of t-butanol : see also Figure 15.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.4	36.03	1.676
	13.0	34.96	1.593
	23.0	33.77	1.504
0.006	30.4	32.95	1.459
	40.7	31.87	1.405
	50.7	30.88	1.365
	60.0	30.02	1.337
(3)	5.4	35.90	1.624
	14.2	34.80	1.549
0.036	27.3	33.29	1.477
	36.8	32.26	1.442
	49.4	31.01	1.410
	60.7	29.96	1.388
(5)	4.9	35.97	1.562
	12.7	34.99	1.549
	21.3	33.97	1.541
0.068	30.8	32.91	1.542
	41.3	31.81	1.546
	51.3	30.82	1.554
	60.3	29.99	1.568
(7)	4.9	35.97	1.922
	13.7	34.87	1.924
0.183	25.8	33.46	1.935
	37.1	32.24	1.945
	48.8	31.06	1.946
	60.1	30.01	1.957
(9)	13.2	34.93	2.491
	22.0	33.89	2.491
0.840	30.1	32.98	2.489
	40.2	31.96	2.488
	50.6	30.89	2.491
	60.2	30.00	2.492

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)	4.6	36.01	1.658
	12.5	35.02	1.587
	23.6	33.71	1.504
0.018	32.0	32.78	1.454
	43.5	31.59	1.400
	50.2	30.93	1.387
	59.1	30.10	1.359
(4)	5.1	35.94	1.548
	13.4	34.91	1.528
0.058	22.4	33.84	1.509
	31.3	32.85	1.501
	49.0	31.05	1.498
	59.5	30.07	1.499
(6)	4.7	36.00	1.672
	13.3	34.92	1.676
	22.0	33.89	1.681
0.102	30.6	32.93	1.687
	40.5	31.89	1.697
	49.6	30.99	1.704
	60.8	29.95	1.716
(8)	4.6	36.01	2.215
	14.2	34.80	2.214
0.356	30.4	32.95	2.213
	39.7	31.97	2.211
	49.8	30.97	2.217
	60.5	29.98	2.223

FIGURE 15 : Solubility curves for argon in aqueous t-butanol of mole fraction x



4. SOLUBILITIES OF OXYGEN

(a) In Water

(i) *Author's results*

t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
3.9	36.10	1.640
6.3	35.79	1.613
10.1	35.32	1.573
13.4	34.93	1.547
20.3	34.09	1.489

(ii) *From Morrison and Billett*[12]

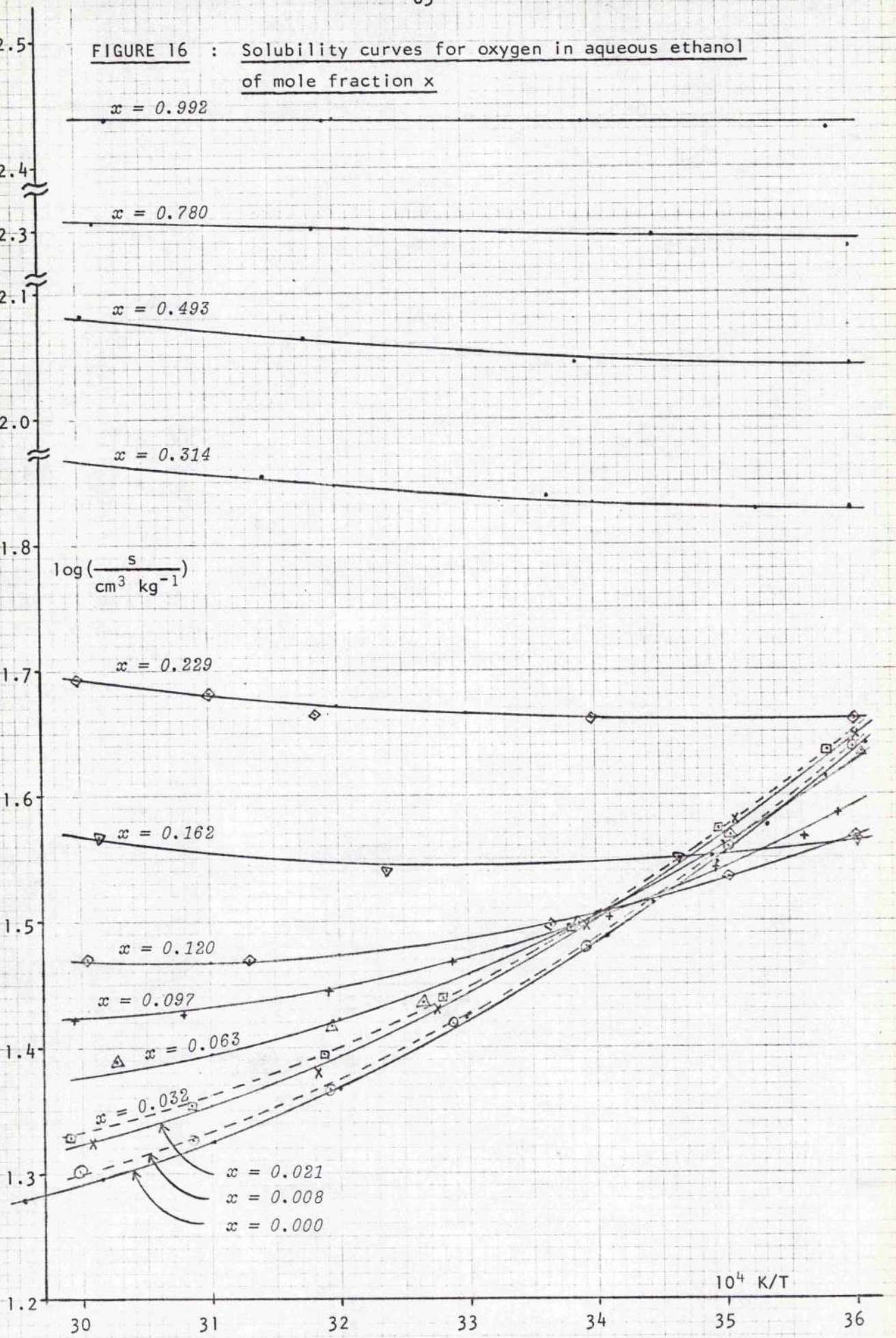
t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
12.7	34.99	1.561
13.5	34.90	1.551
17.3	34.43	1.513
21.5	33.94	1.479
30.0	32.99	1.423
39.4	32.00	1.368
49.3	31.02	1.324
58.5	30.16	1.296
65.3	29.55	1.279

(b) In aqueous ethanol, for the following mole fractions (x) of ethanol ; see also Figure 16.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.7	36.00	1.638
	12.5	35.02	1.558
	21.8	33.91	1.480
0.008	31.0	32.88	1.419
	40.2	31.92	1.364
	51.0	30.85	1.326
	60.5	29.98	1.301
(3)	6.2	35.80	1.635
	13.0	34.96	1.572
	22.8	33.80	1.494
0.032	31.7	32.80	1.439
	40.7	31.87	1.395
	51.1	30.84	1.353
	61.4	29.90	1.329
	5.6	35.88	1.586
(5)	7.7	35.61	1.568
	13.2	34.93	1.542
0.097	20.2	34.10	1.502
	31.1	32.87	1.468
	40.3	31.91	1.444
	51.6	30.79	1.427
	60.9	29.94	1.422
	4.4	36.03	1.564
(7)	15.5	34.65	1.550
0.162	35.7	32.38	1.540
	58.8	30.13	1.568
(9)	4.7	36.00	1.829
0.314	10.4	35.28	1.828
	25.1	33.55	1.839
	45.2	31.42	1.853
(11)	4.6	36.01	2.287
0.780	21.2	33.98	2.296
	41.1	31.83	2.301
	58.8	30.13	2.306

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)	4.6	36.01	1.648
	12.0	35.08	1.580
	21.8	33.91	1.497
0.021	32.2	32.76	1.430
	41.2	31.82	1.379
	59.3	30.08	1.325
	4.1	36.07	1.633
(4)	12.3	35.04	1.569
	22.2	33.87	1.498
0.063	33.2	32.65	1.435
	40.2	31.92	1.418
	57.2	30.27	1.389
	4.6	36.01	1.568
(6)	12.4	35.03	1.535
	24.3	33.63	1.496
0.120	46.4	31.30	1.469
	59.8	30.04	1.470
	4.6	36.01	1.660
(8)	21.2	33.98	1.661
0.229	41.2	31.82	1.665
	49.4	31.01	1.681
	60.3	29.99	1.692
(10)	4.6	36.01	2.041
0.493	22.2	33.87	2.044
	41.7	31.77	2.063
	60.0	30.02	2.081
(12)	5.8	35.85	2.430
0.992	21.7	33.92	2.437
	40.2	31.92	2.438
	57.7	30.23	2.439

FIGURE 16 : Solubility curves for oxygen in aqueous ethanol of mole fraction x

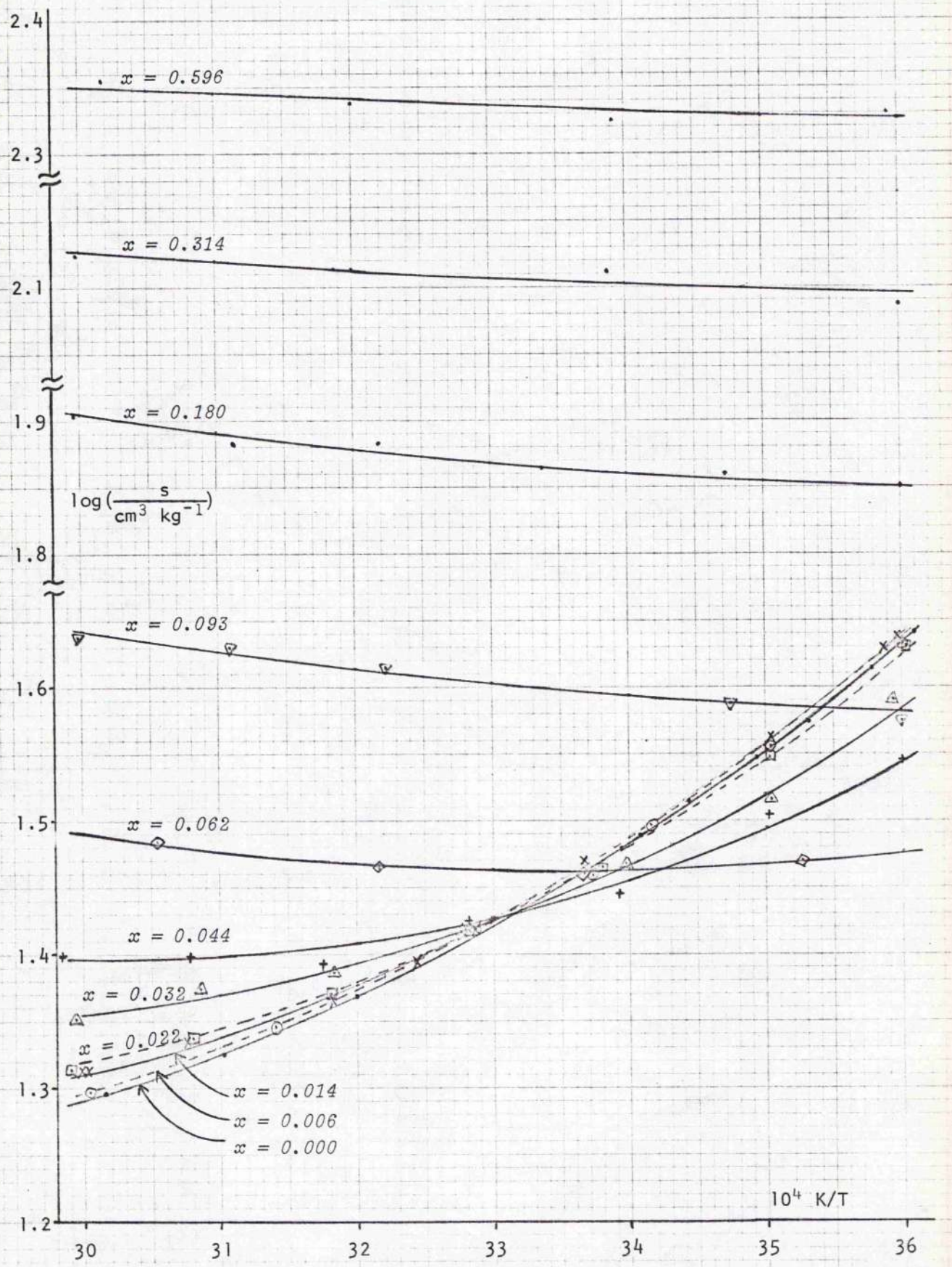


(c) In aqueous t-butanol, for the following mole fractions (x) of t-butanol : see also Figure 17.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.6	36.01	1.631
	12.4	35.03	1.554
	19.7	34.16	1.495
0.006	23.4	33.72	1.459
	31.1	32.87	1.419
	45.4	31.40	1.344
	59.8	30.04	1.296
	4.4	36.03	1.630
(3)	12.5	35.02	1.548
	22.8	33.80	1.466
0.022	31.6	32.82	1.418
	41.3	31.81	1.370
	51.5	30.80	1.338
	61.4	29.90	1.313
	4.7	36.00	1.545
(5)	12.9	35.02	1.504
	21.7	33.92	1.446
0.044	31.6	32.82	1.424
	41.8	31.76	1.393
	51.6	30.79	1.398
	62.0	29.84	1.399
	4.7	36.00	1.575
(7)	14.7	34.74	1.588
0.093	37.3	32.22	1.614
	48.5	31.09	1.630
	60.4	29.98	1.638
(9)	4.7	36.00	2.087
0.314	22.2	33.87	2.111
	40.7	31.87	2.113
	60.3	29.99	2.124

x	t/°C	10^4 K/T	log(s/cm^3.kg^{-1})
(2)	4.8	35.98	1.638
	5.7	35.87	1.629
	12.5	35.03	1.563
0.014	23.9	33.67	1.469
	31.1	32.87	1.417
	35.3	32.43	1.392
	41.3	31.81	1.366
	52.1	30.75	1.336
	59.9	30.03	1.312
	60.4	29.99	1.312
	5.2	35.93	1.590
(4)	12.4	35.03	1.517
	21.2	33.98	1.469
0.032	32.1	32.77	1.416
	41.2	31.82	1.386
	51.0	30.85	1.373
	60.9	29.94	1.351
(6)	10.5	35.27	1.470
	23.8	33.68	1.460
0.062	37.8	32.17	1.467
	54.4	30.54	1.483
	4.6	36.01	1.850
(8)	15.0	34.71	1.860
0.180	26.4	33.38	1.864
	37.6	32.19	1.882
	48.3	31.11	1.882
	60.6	29.97	1.904
(10)	5.3	35.92	2.331
0.596	21.8	33.91	2.325
	39.4	32.00	2.338
	58.3	30.17	2.354

FIGURE 17 : Solubility curves for oxygen in aqueous t-butanol of mole fraction x



5. SOLUBILITIES OF CARBON DIOXIDE

(a) In Water

(i) *Author's results*

t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
4.5	36.02	3.159
6.4	35.77	3.128
9.9	35.34	3.074
24.7	33.58	2.882
40.2	31.92	2.721
55.1	30.47	2.609
60.0	30.02	2.575

(ii) *From Morrison and Billett*[12]

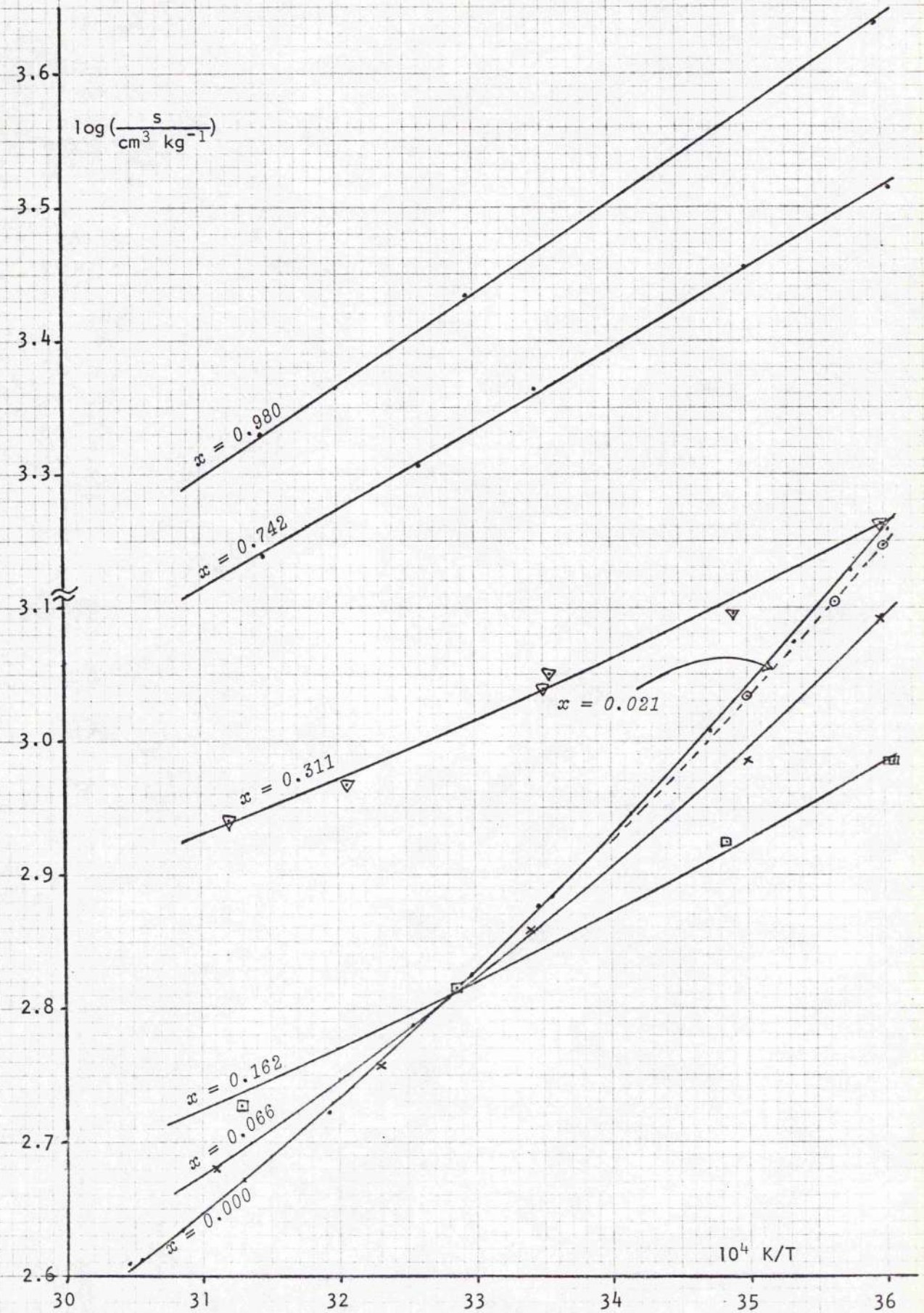
t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
14.9	34.72	3.008
19.8	34.14	2.945
25.8	33.46	2.876
30.3	32.96	2.823
34.3	32.53	2.787
46.4	31.30	2.671
51.1	30.84	2.633
54.3	30.55	2.611
63.1	29.74	2.546

(b) In aqueous ethanol, for the following mole fractions (x) of ethanol : *unpublished results of T.J. Morrison* : see also Figure 18.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.6	36.00	3.148
0.021	7.5	35.65	3.103
	12.7	35.00	3.032
(3)	4.2	36.07	2.986
	4.4	36.03	2.986
0.162	13.9	34.84	2.924
	31.3	32.85	2.813
	46.5	31.29	2.728
(5)	4.3	36.05	3.515
	12.5	35.00	3.455
0.742	25.9	33.45	3.363
	33.7	32.60	3.307
	44.7	31.46	3.239

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)	4.8	35.98	3.092
	12.7	35.00	2.985
0.066	26.4	33.40	2.859
	36.9	32.30	2.757
	48.6	31.10	2.680
(4)	4.9	35.97	3.163
	14.1	34.90	3.096
0.311	25.0	33.55	3.050
	25.7	33.50	3.039
	39.0	32.06	2.968
	48.4	31.20	2.940
(6)	5.1	35.95	3.638
	30.5	32.94	3.434
0.980	44.9	31.45	3.330

FIGURE 18 : Solubility curves for carbon dioxide in aqueous ethanol of mole fraction x

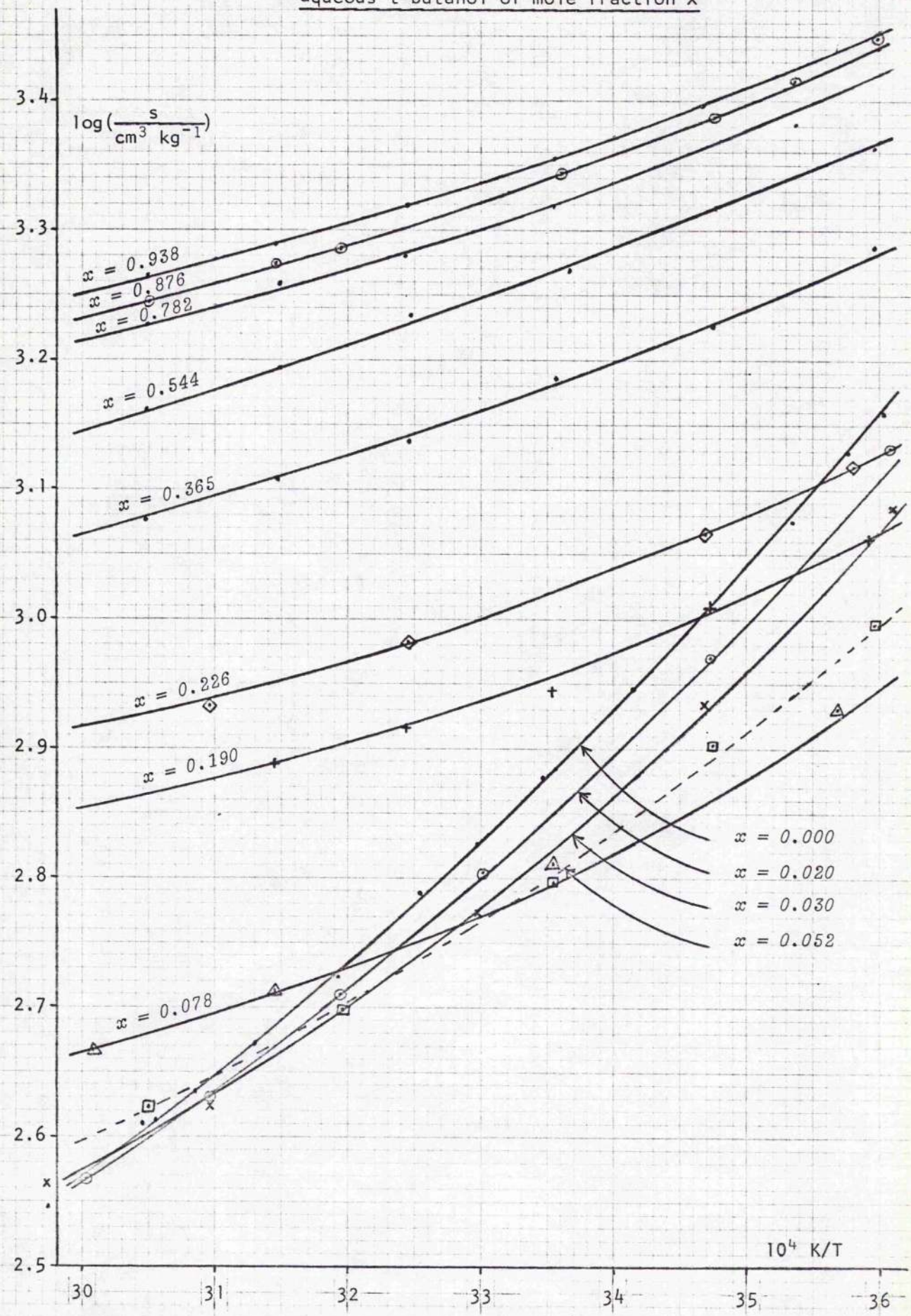


(c) In aqueous t-butanol for the following mole fractions (x) of t-butanol : *unpublished results of T.J. Morrison, except for numbers 7, 8, 9, and 10, determined by the author* : see also Figure 19.

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(1)	4.0	36.08	3.132
	14.9	34.72	2.970
0.020	29.9	33.01	2.804
	40.2	31.93	2.710
	50.0	30.97	2.630
	60.0	30.02	2.568
(3)	4.9	35.97	2.996
	14.7	34.74	2.902
0.052	25.1	33.54	2.797
	40.0	31.95	2.698
	54.8	30.50	2.621
(5)	5.4	35.91	3.062
	14.9	34.72	3.009
0.190	25.2	33.53	2.945
	35.2	32.43	2.917
	44.9	31.45	2.888
(7)	5.0	35.96	3.287
	14.8	34.73	3.226
0.365	24.8	33.57	3.186
	35.0	32.46	3.138
	44.6	31.48	3.109
	55.0	30.48	3.077
(9)	9.7	35.37	3.381
	25.1	33.54	3.319
0.782	35.3	32.42	3.280
	44.4	31.49	3.259
	54.9	30.49	3.228
(11)	15.3	34.67	3.396
	25.1	33.54	3.354
0.938	35.1	32.44	3.319
	44.9	31.45	3.289
	54.9	30.49	3.262

x	t/°C	10^4 K/T	log(s/cm^3 kg^{-1})
(2)	3.9	36.10	3.086
	15.0	34.69	2.934
0.030	30.1	32.98	2.773
	49.9	30.96	2.625
	63.3	29.73	2.564
	74.1	28.80	2.485
(4)	7.1	35.69	2.930
	25.1	33.54	2.811
0.078	44.9	31.45	2.712
	59.4	30.08	2.666
(6)	6.2	35.80	3.119
	15.1	34.69	3.067
0.226	35.1	32.45	2.982
	49.9	30.96	2.932
(8)	5.0	35.96	3.363
	14.5	34.77	3.318
	24.9	33.56	3.269
0.544	34.9	32.47	3.234
	44.5	31.49	3.193
	55.0	30.48	3.161
(10)	4.7	35.99	3.449
	9.7	35.37	3.416
0.876	14.6	34.75	3.387
	24.5	33.60	3.343
	39.8	31.94	3.285
	44.9	31.45	3.274
	54.8	30.50	3.245

FIGURE 19 : Solubility curves for carbon dioxide in aqueous t-butanol of mole fraction x



CHAPTER 5 DISCUSSION OF RESULTS

1. PRESENTATION OF GRAPHS

The five gases have been used as probes to investigate the effects of ethanol and t-butanol on the structure of water. So for each gas in turn graphs have been drawn to show the variation in several parameters with increasing mole fraction of alcohol. To facilitate comparison, the variations for both alcohols are presented on the same diagrams. (For many of the t-butanol systems, extrapolation beyond $x = 0.6$ has been carried out since experimental results are scarce for higher concentrations of this alcohol, due to its high viscosity and freezing point.)

(a) Solubility isotherms : Figures 20-27

The solubility increases by a factor of about ten when passing from pure water to the pure alcohol. This is shown in Figures 20, 21, and 22 for three different temperatures, over the whole concentration range of the solvent. It was found that the solubilities change most significantly, and with an interesting oscillation, over the lower concentrations. Figures 23-27 therefore give isotherms on an expanded scale for $x = 0 \rightarrow 0.3$. For clarity, intermediate isotherms for t-butanol solutions are omitted, but the transition from one isotherm to the next is smooth, as shown by the corresponding curves for the ethanol solutions.

(b) $\Delta\bar{G}^\circ$ isotherms : Figures 28-32

Since $\Delta\bar{G}^\circ = -2.303RT \log x_A$,

or $\Delta\bar{G}^\circ = +2.303RT[4.35 + \log(n_B + n_C) - \log s]$,

the variation in $\Delta\bar{G}^\circ$ follows that in log s although in the opposite direction. These isotherms do not cross one another, as many of the log s isotherms do, so that interpretation is made easier, and temperature effects may be more easily identified. They are presented in Figures 28-32 for the whole concentration range of solvent, and again the intermediate isotherms for t-butanol solutions are omitted. The plotting of these isotherms is consistent with the possible error of 0.5% in $\Delta\bar{G}^\circ$, and all points fall on the lines, although this is not shown to avoid congestion.

(c) $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ isotherms : Figures 33-37

For each gas, $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ isotherms are drawn on the same graph to show how closely their variations resemble one another. When interpreting these, however, the possible error of 2-3% must be borne in mind, and in fact the isotherms have been smoothed out through a small amount of scatter in the these points, although again not all of these are shown.

(d) $\Delta\bar{C}_p^\circ$ isotherms : Figures 38-39

$\Delta\bar{C}_p^\circ$ for the solubility of the different gases has been estimated. It decreases as temperature rises, but is approximately constant over the intervals 10-25°C, and 30-50°C. Its possible error is large ($\sim$10 J K^{-1}) throughout, but an indication of its dependence on mole fraction of alcohol is given in figures 38-39. This dependence was found to be linear from $x \fallingdotseq 0.4 \rightarrow 1.0$, and graphs have been discontinued at $x \fallingdotseq 0.8$.

FIGURE 20 : Solubility isotherms for HELIUM and OXYGEN in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

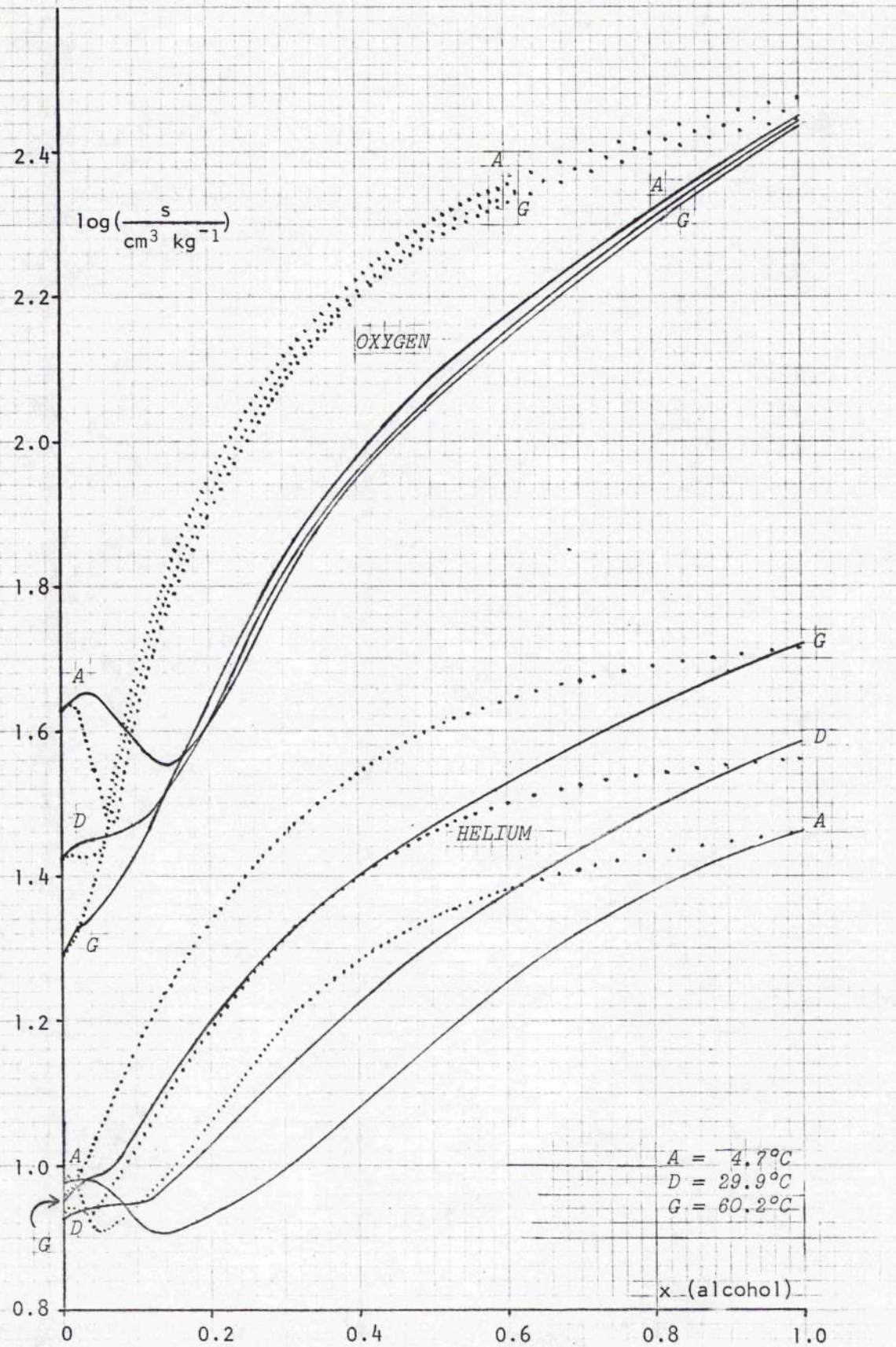


FIGURE 21 : Solubility isotherms for HYDROGEN and CARBON DIOXIDE in aqueous alcohols of mole fraction x

ethanol - full lines;
t-butanol - broken lines.

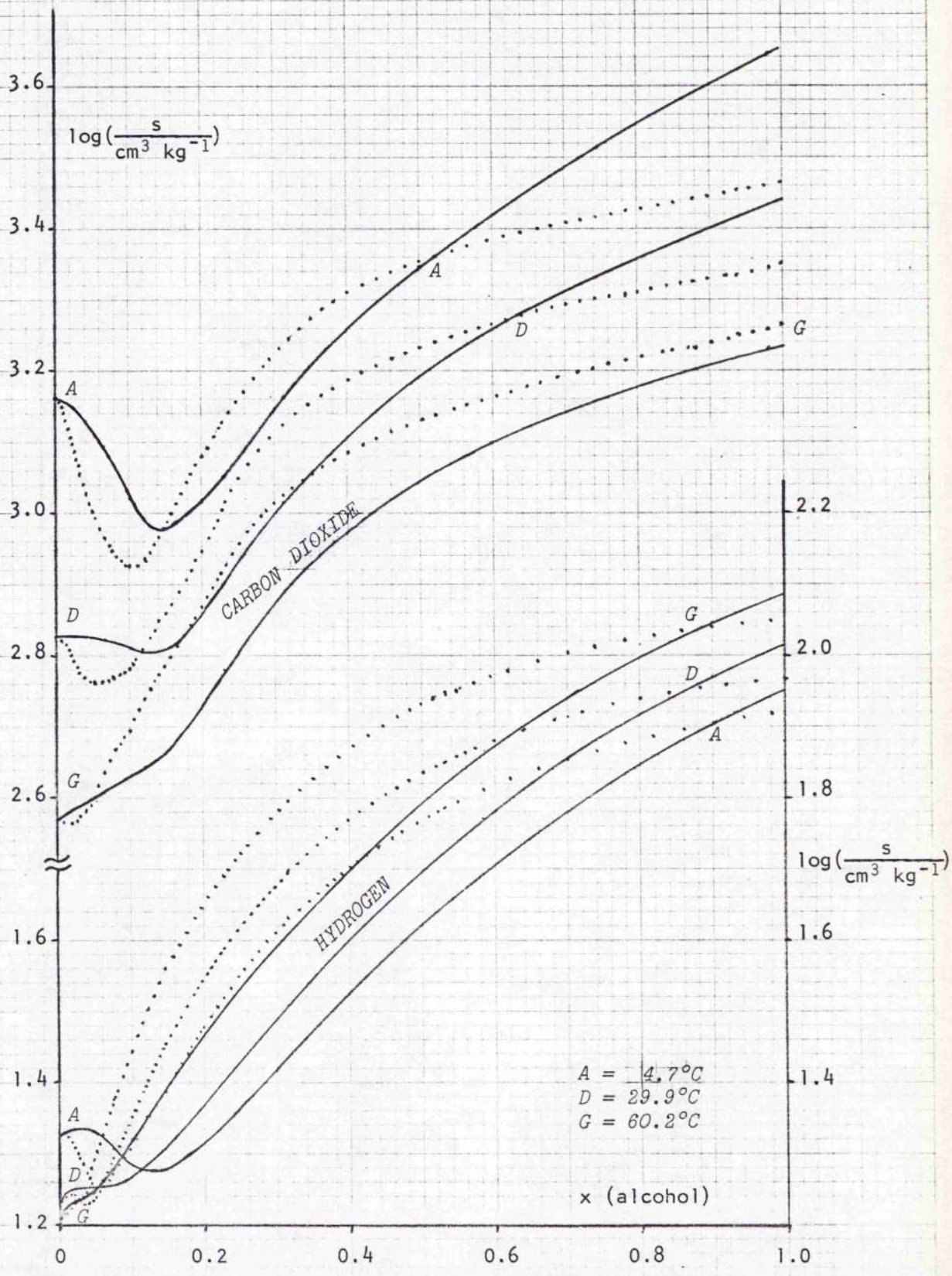


FIGURE 22 : Solubility isotherms for ARGON in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

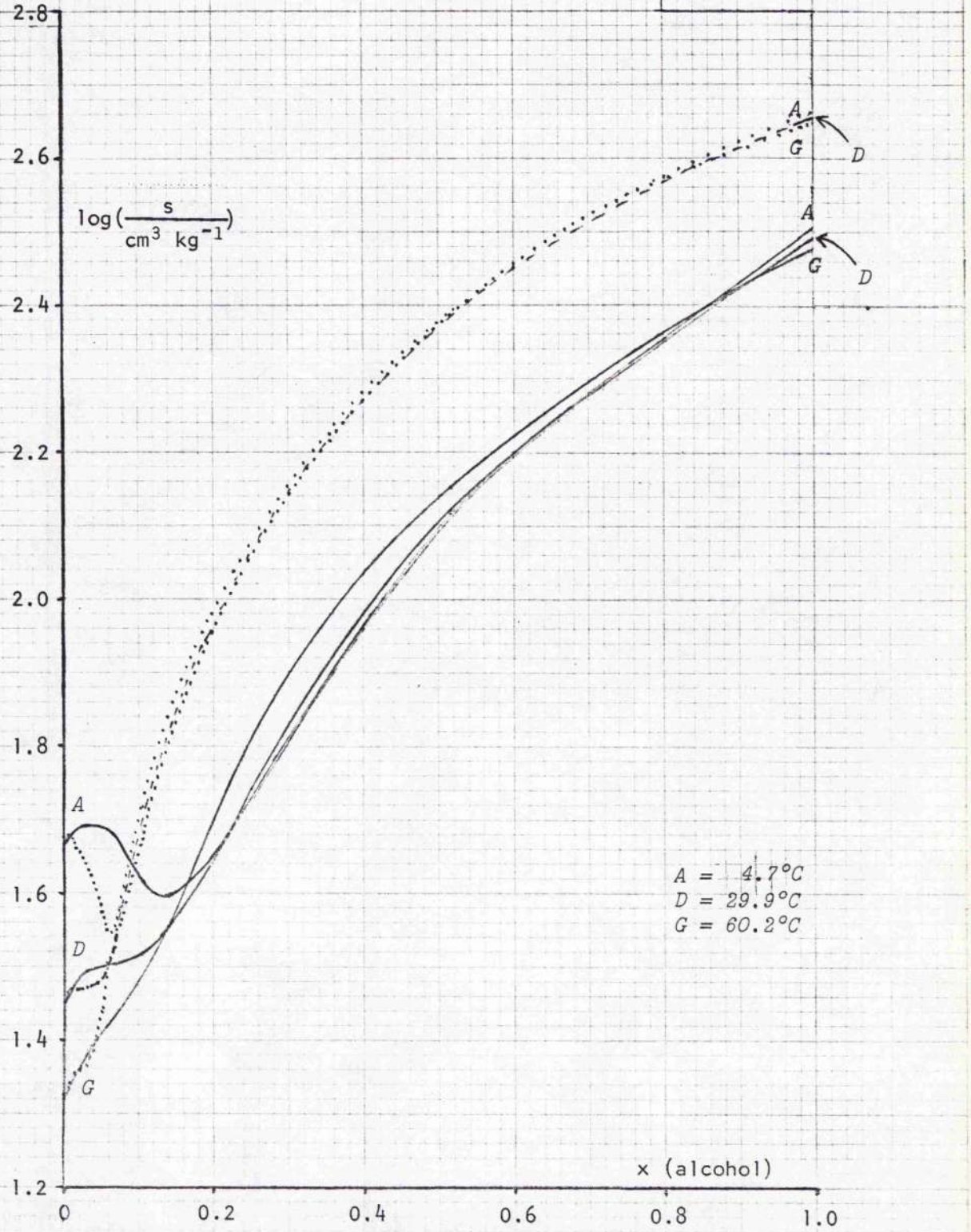


FIGURE 23 : Solubility isotherms for HELIUM in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

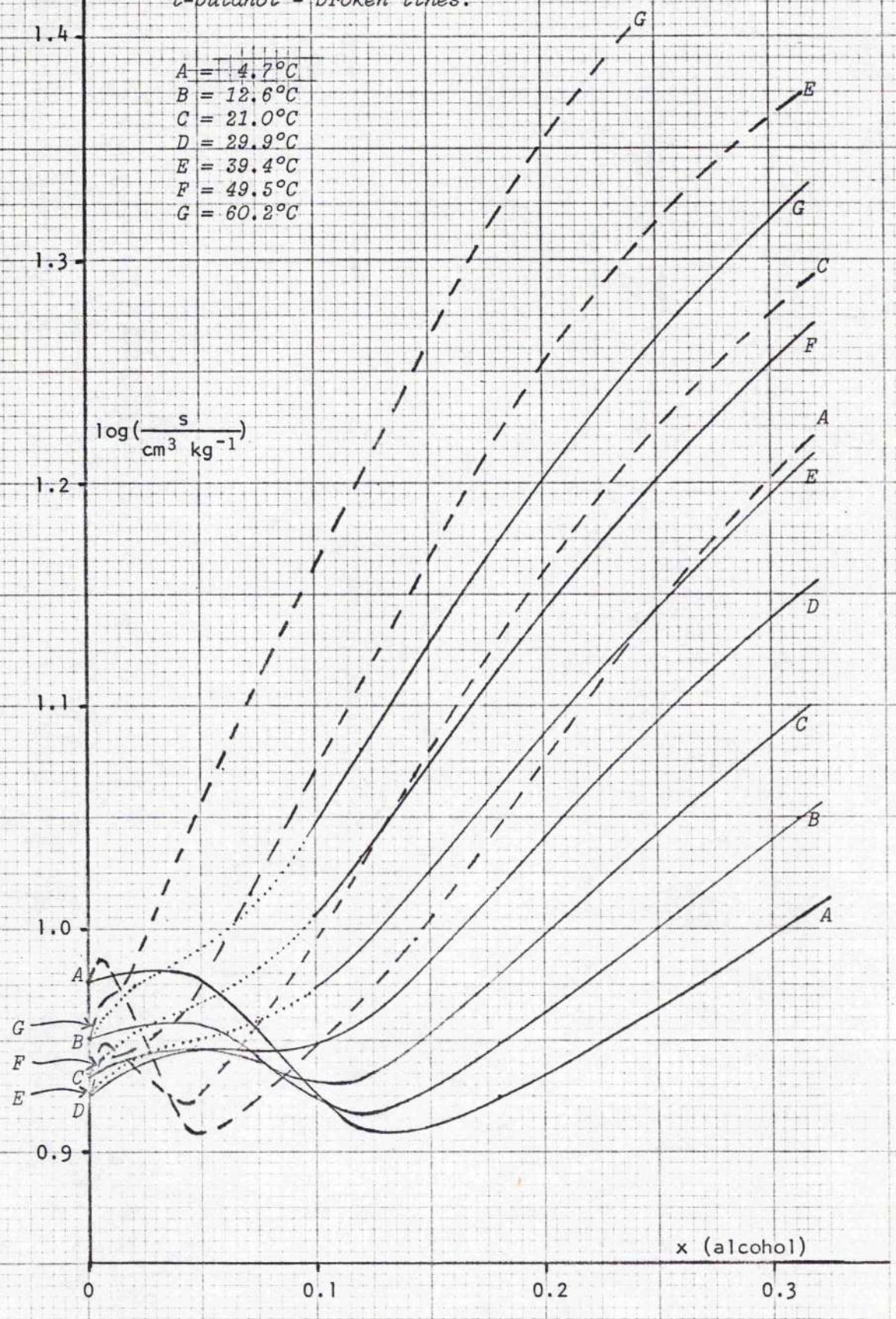


FIGURE 24 : Solubility isotherms for HYDROGEN in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

A = 4.7°C
B = 12.6°C
C = 21.0°C
D = 29.9°C
E = 39.4°C
F = 49.5°C
G = 60.2°C

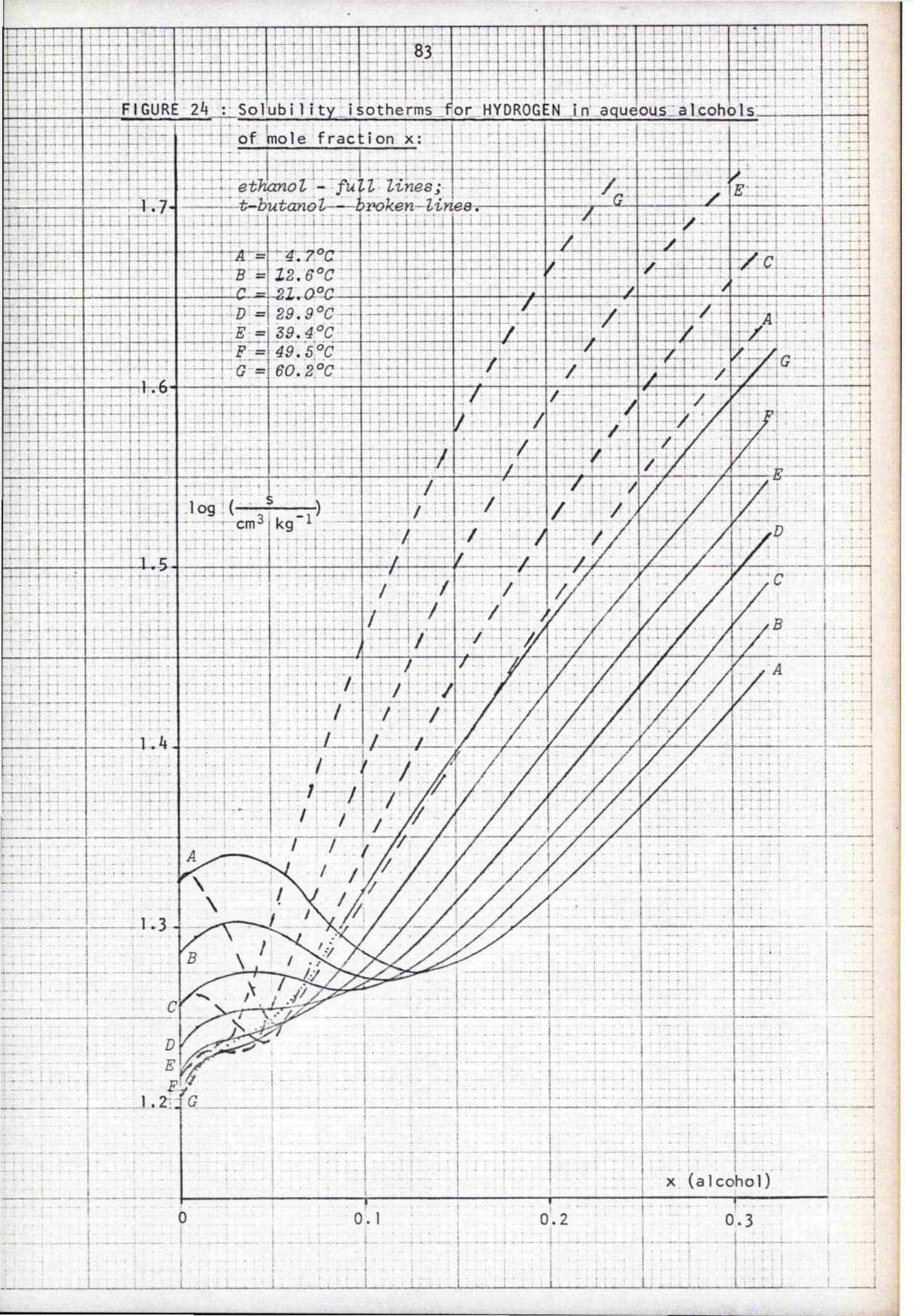


FIGURE 25 : Solubility isotherms for ARGON in aqueous alcohols of mole fraction x:

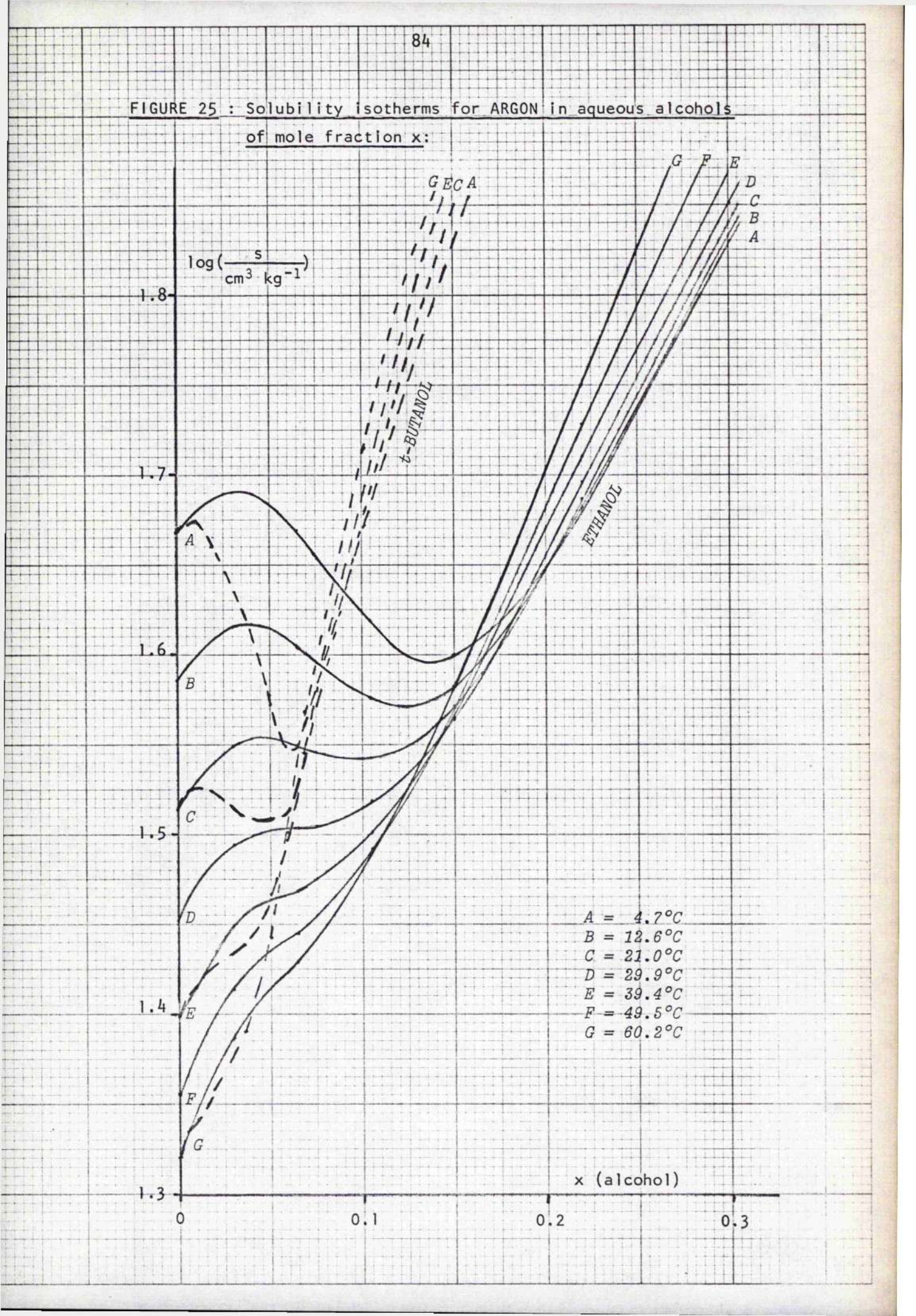


FIGURE 26 : Solubility isotherms for OXYGEN in aqueous alcohols of mole fraction x:

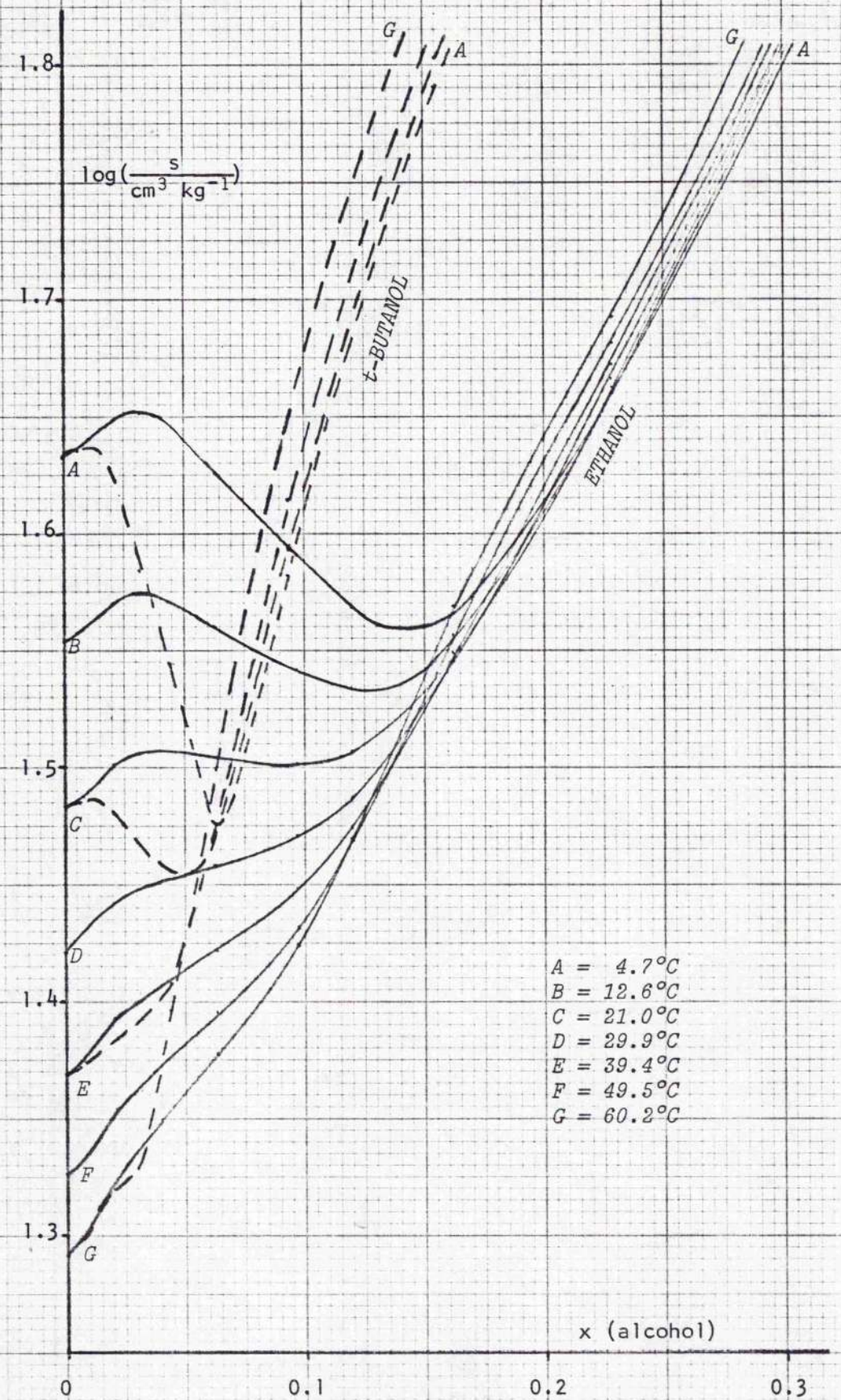


FIGURE 27 : Solubility isotherms for CARBON DIOXIDE in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

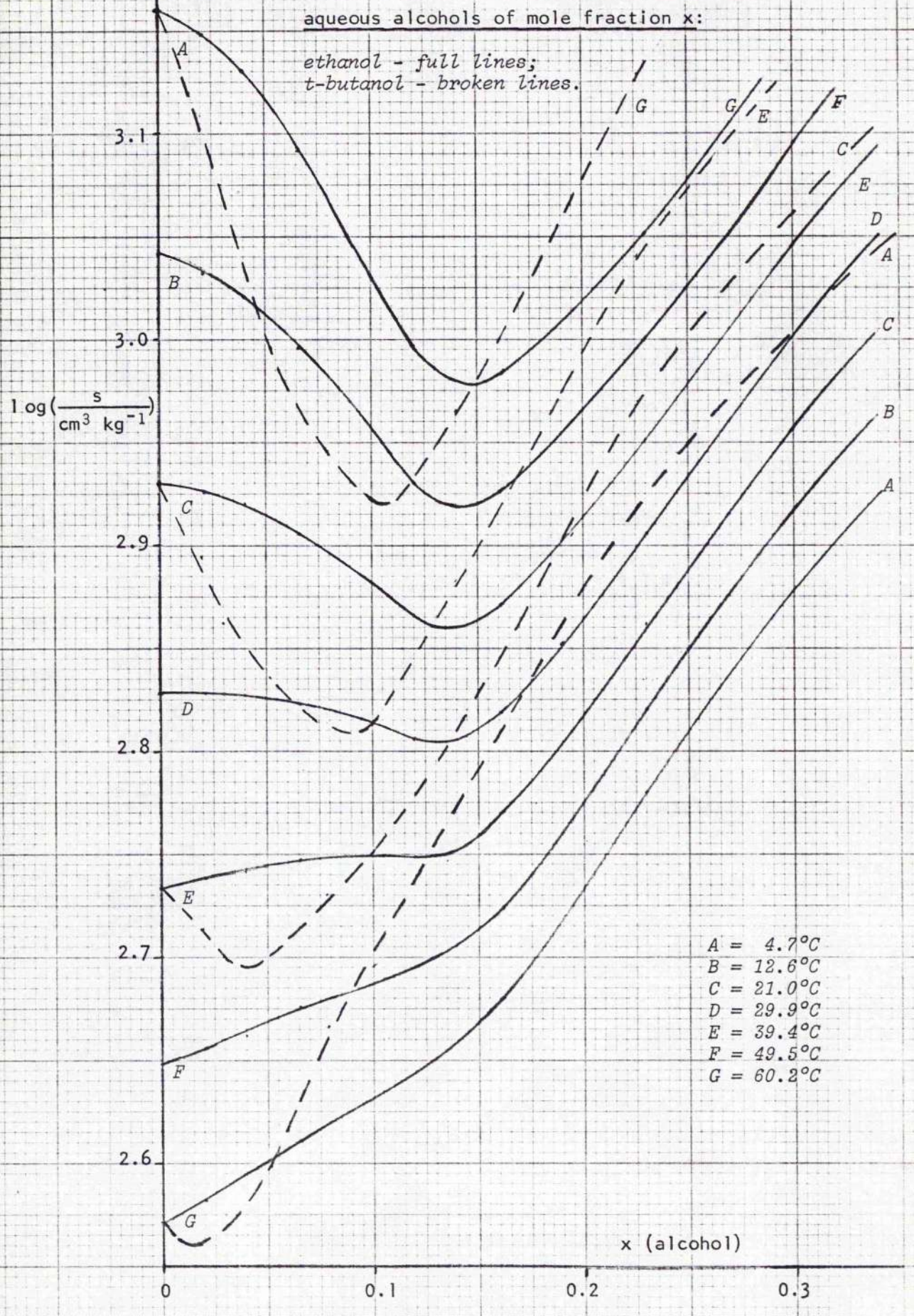


FIGURE 28 : $\bar{\Delta G}^\circ$ isotherms for solubility of HELIUM in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

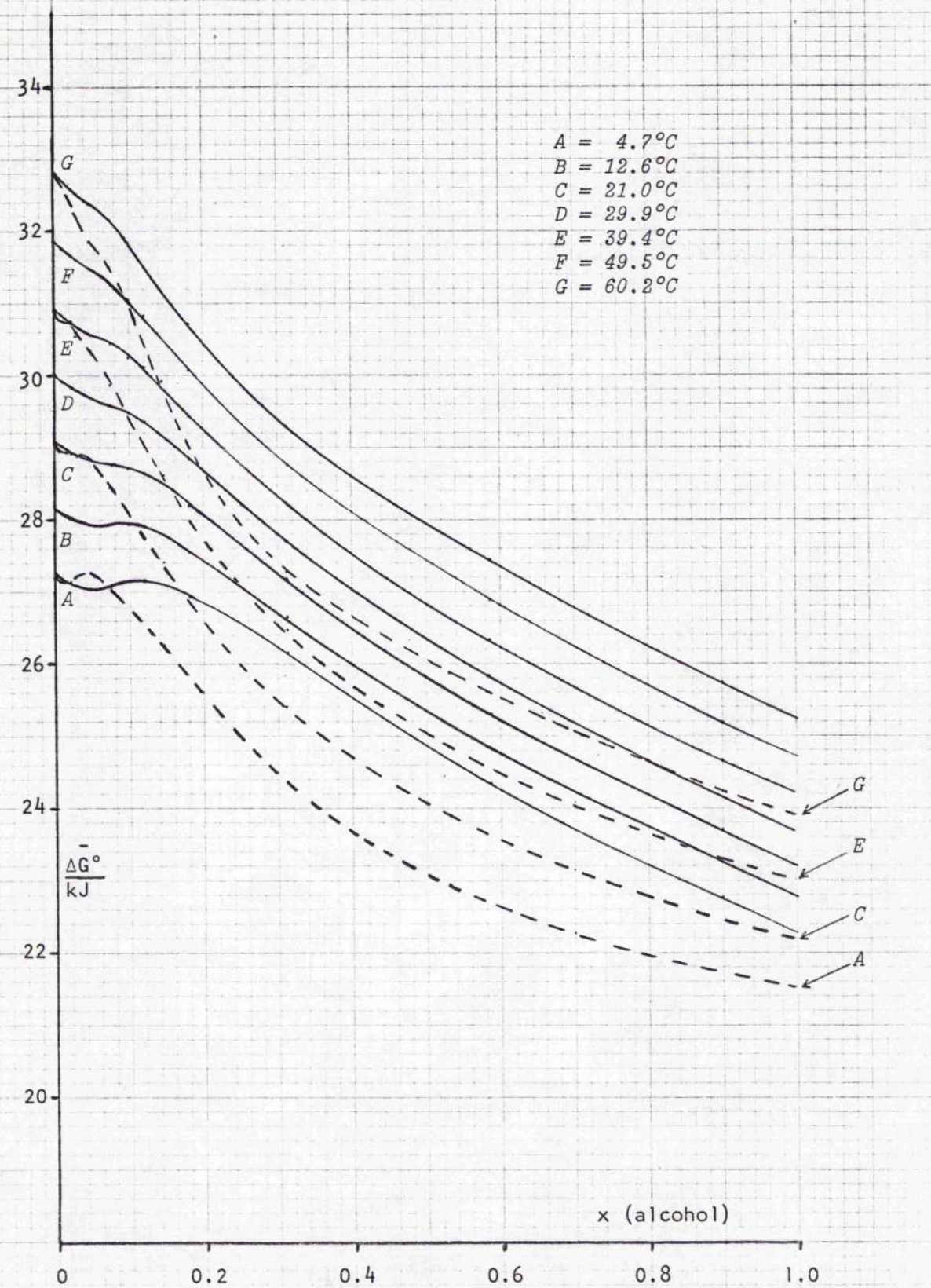


FIGURE 29 : $\bar{\Delta G}^\circ$ isotherms for solubility of HYDROGEN in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

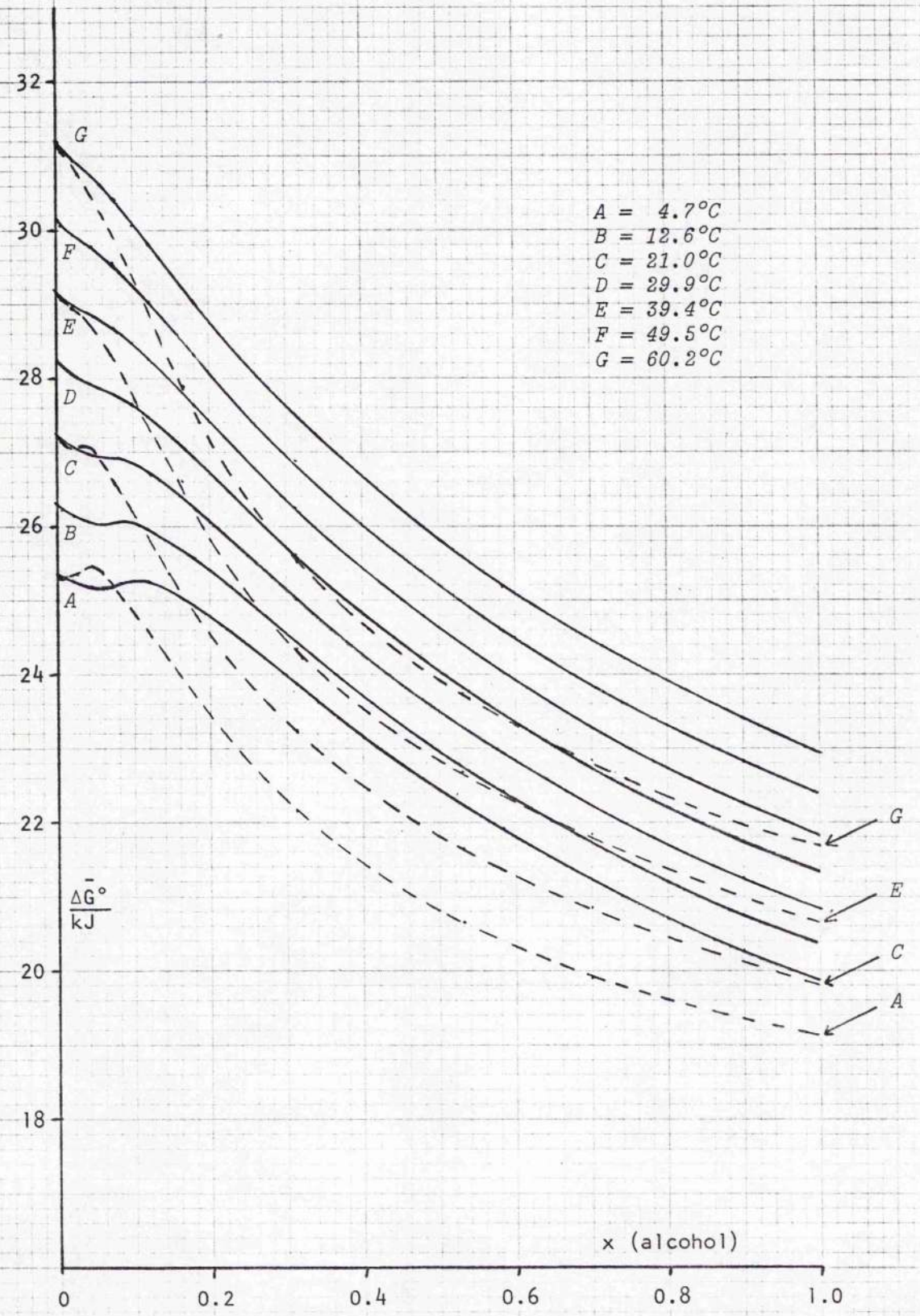


FIGURE 30 : $\bar{\Delta G}^\circ$ isotherms for solubility of ARGON in aqueous alcohols of mole fraction x:

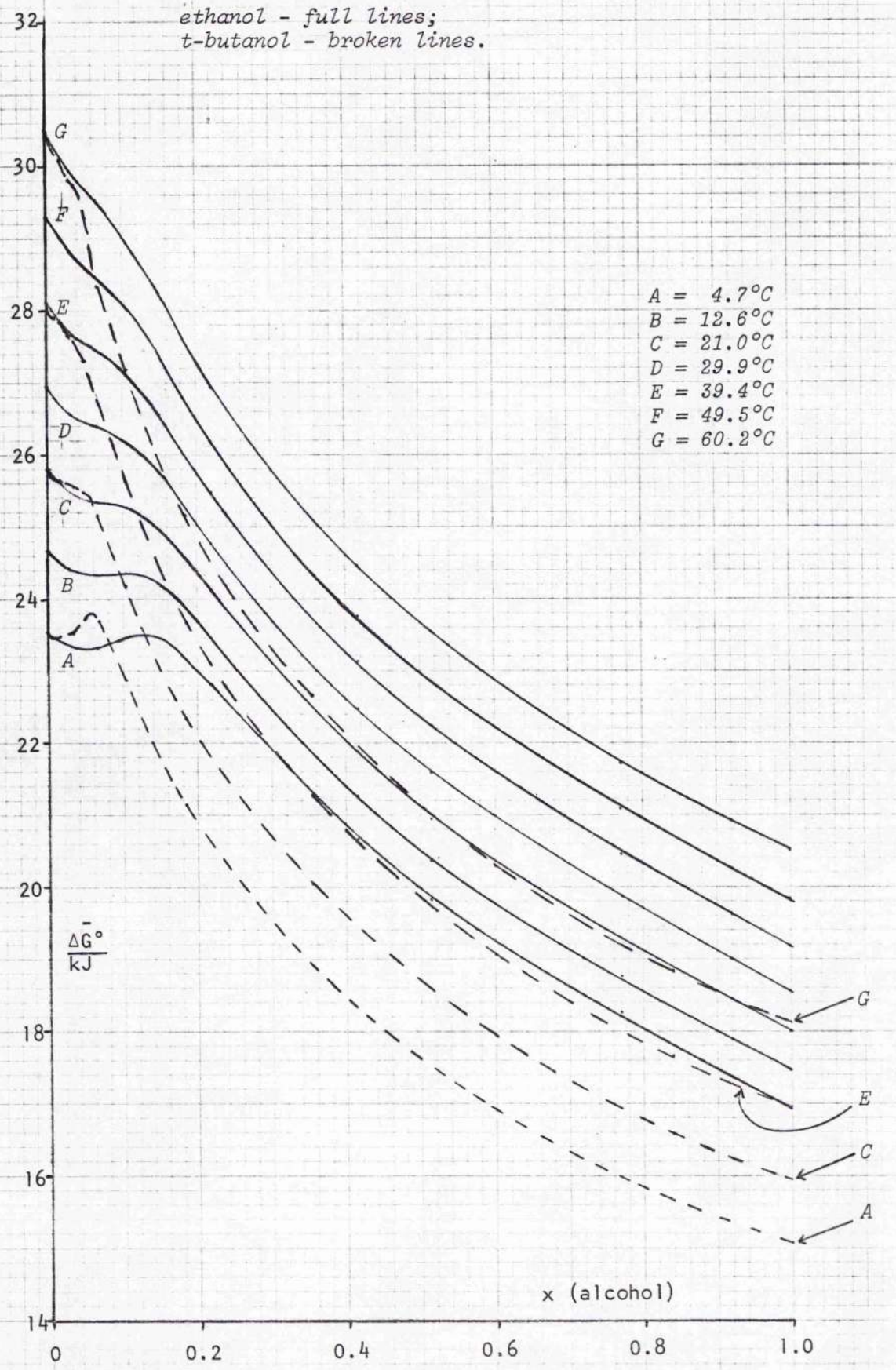


FIGURE 31 : $\bar{\Delta G}^\circ$ isotherms for solubility of OXYGEN in aqueous alcohols of mole fraction x:

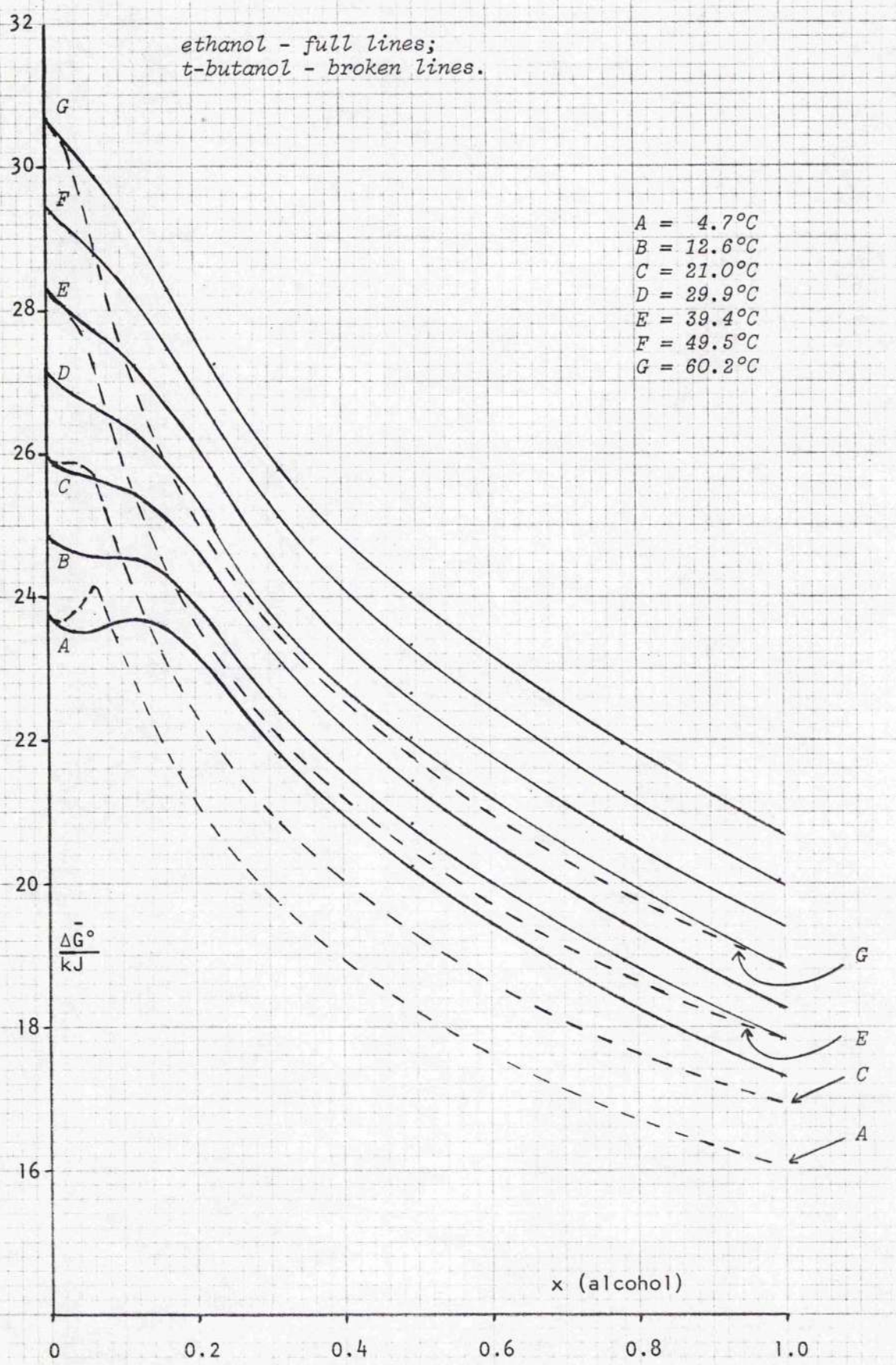


FIGURE 32 : $\bar{\Delta G}^\circ$ isotherms for solubility of CARBON DIOXIDE in aqueous alcohols of mole fraction x:

ethanol - full lines;
t-butanol - broken lines.

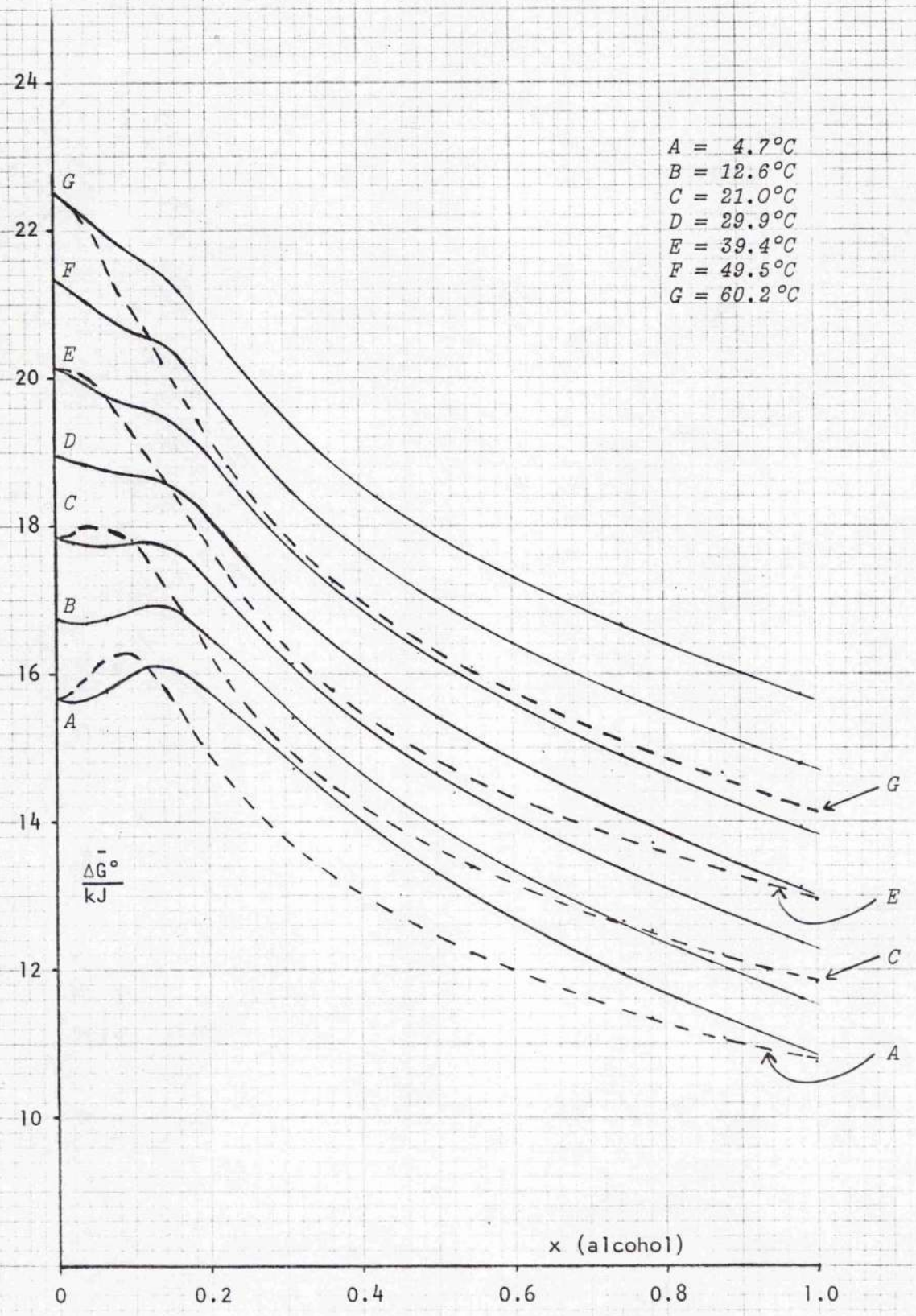


FIGURE 33 : $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ isotherms for solubility of HELIUM in aqueous alcohols of mole fraction x:

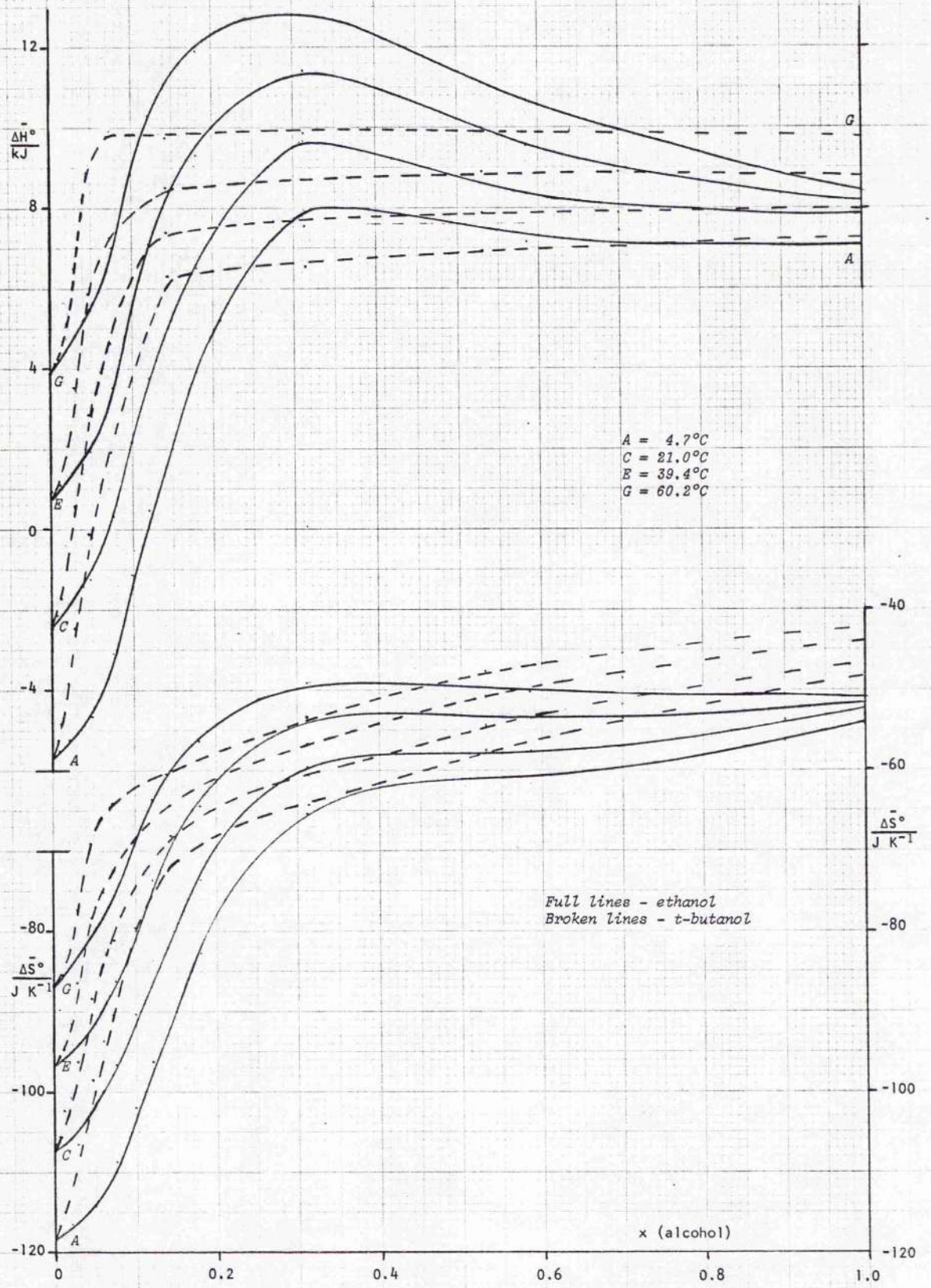


FIGURE 34 : $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ isotherms for solubility of HYDROGEN in aqueous alcohols of mole fraction x:

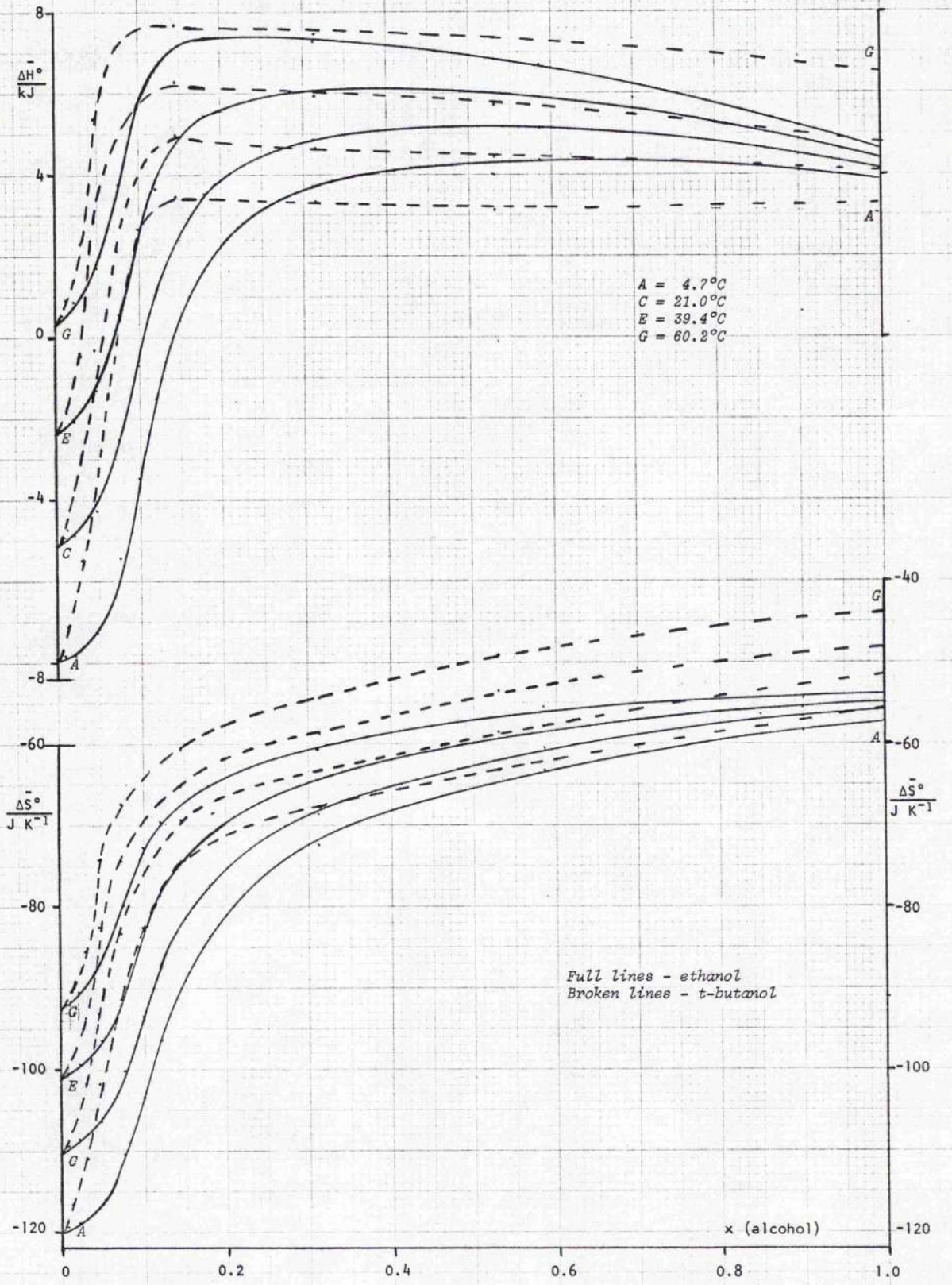


FIGURE 35 : $\bar{\Delta}H°$ and $\bar{\Delta}S°$ for solubility of ARGON in aqueous alcohols of mole fraction x

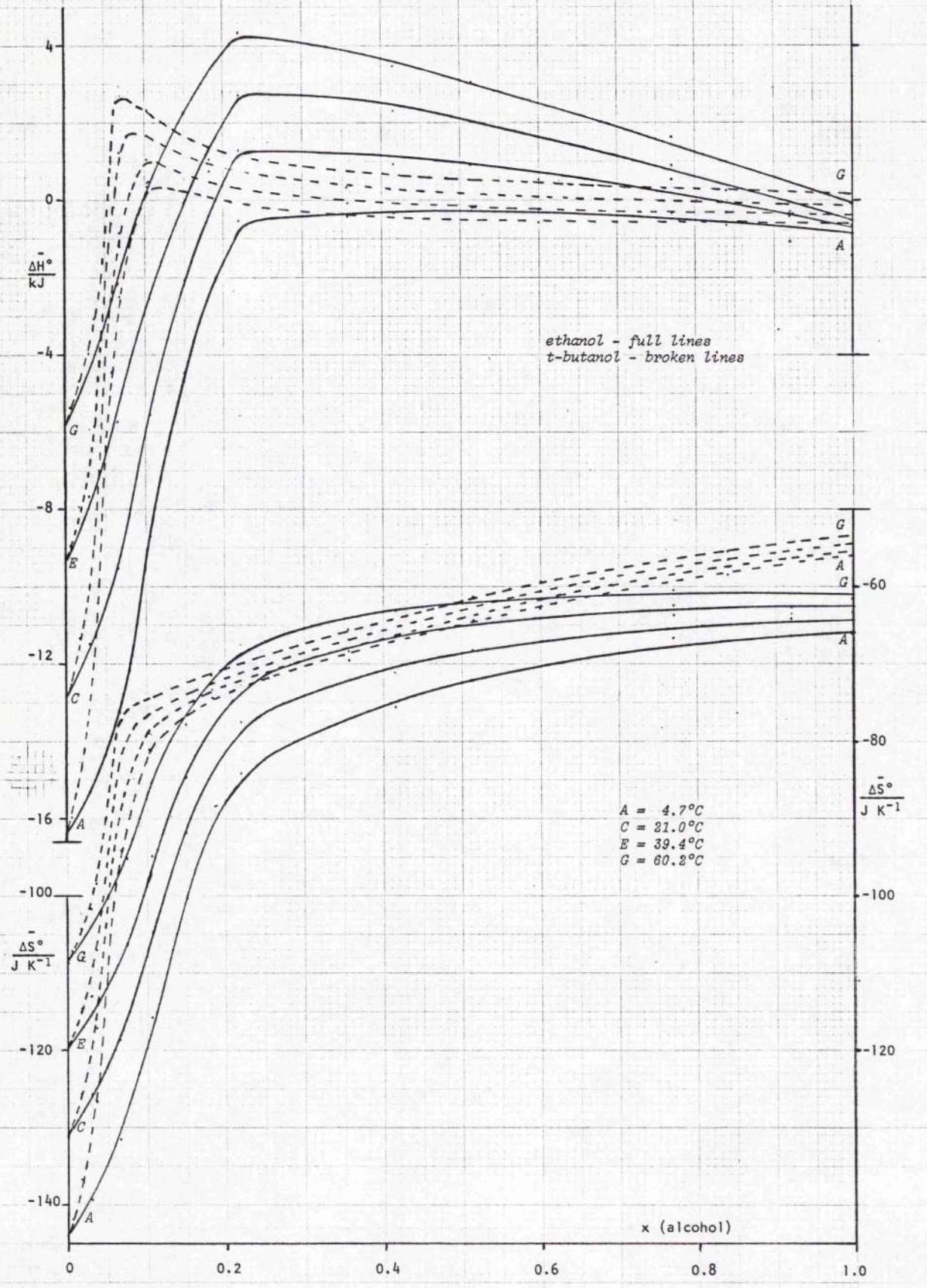


FIGURE 36 : $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ for solubility of OXYGEN in aqueous alcohols of mole fraction x:

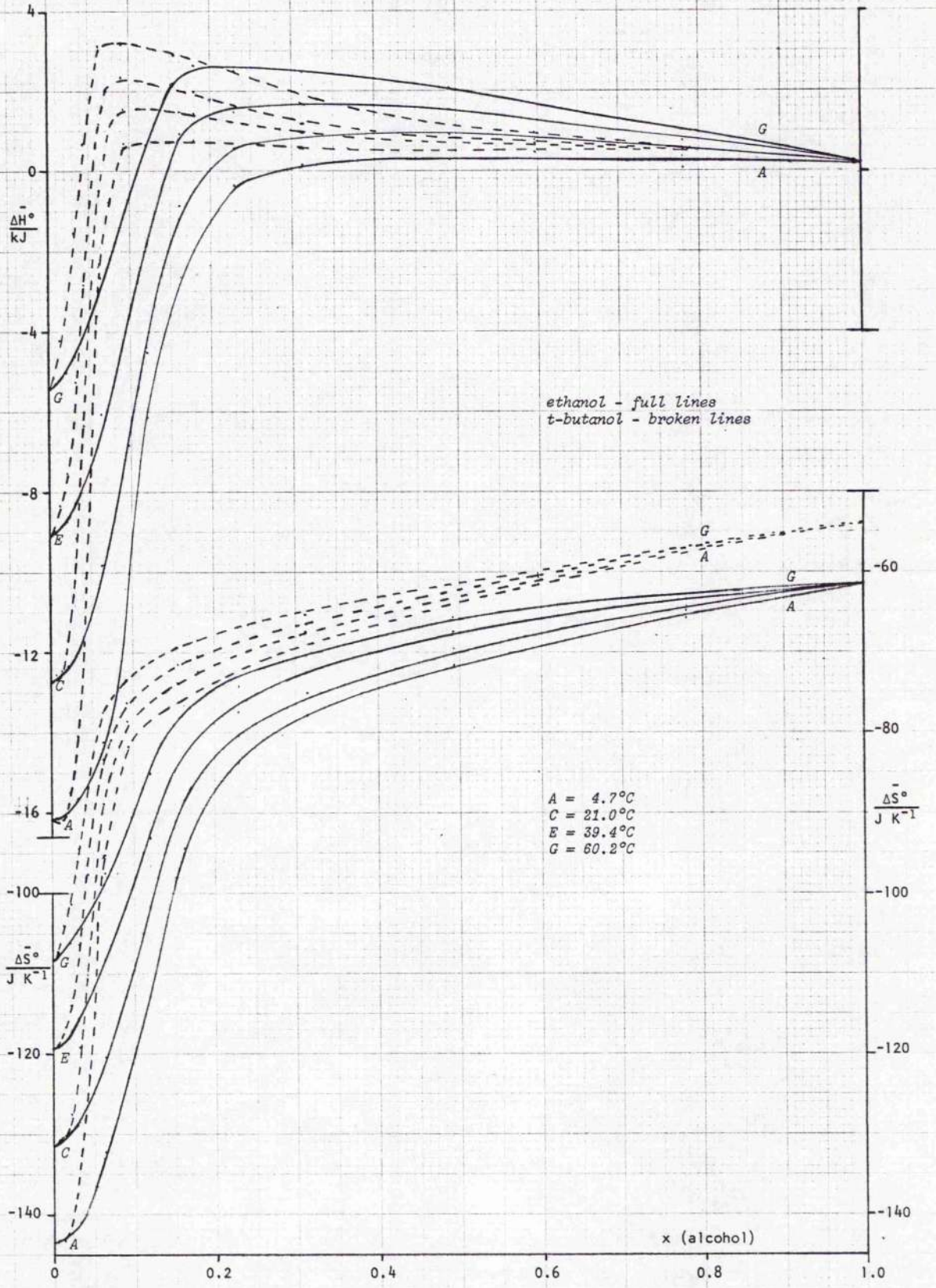


FIGURE 37 : $\Delta\bar{H}°$ and $\Delta\bar{S}°$ for solubility of CARBON DIOXIDE in aqueous alcohols of mole fraction x:

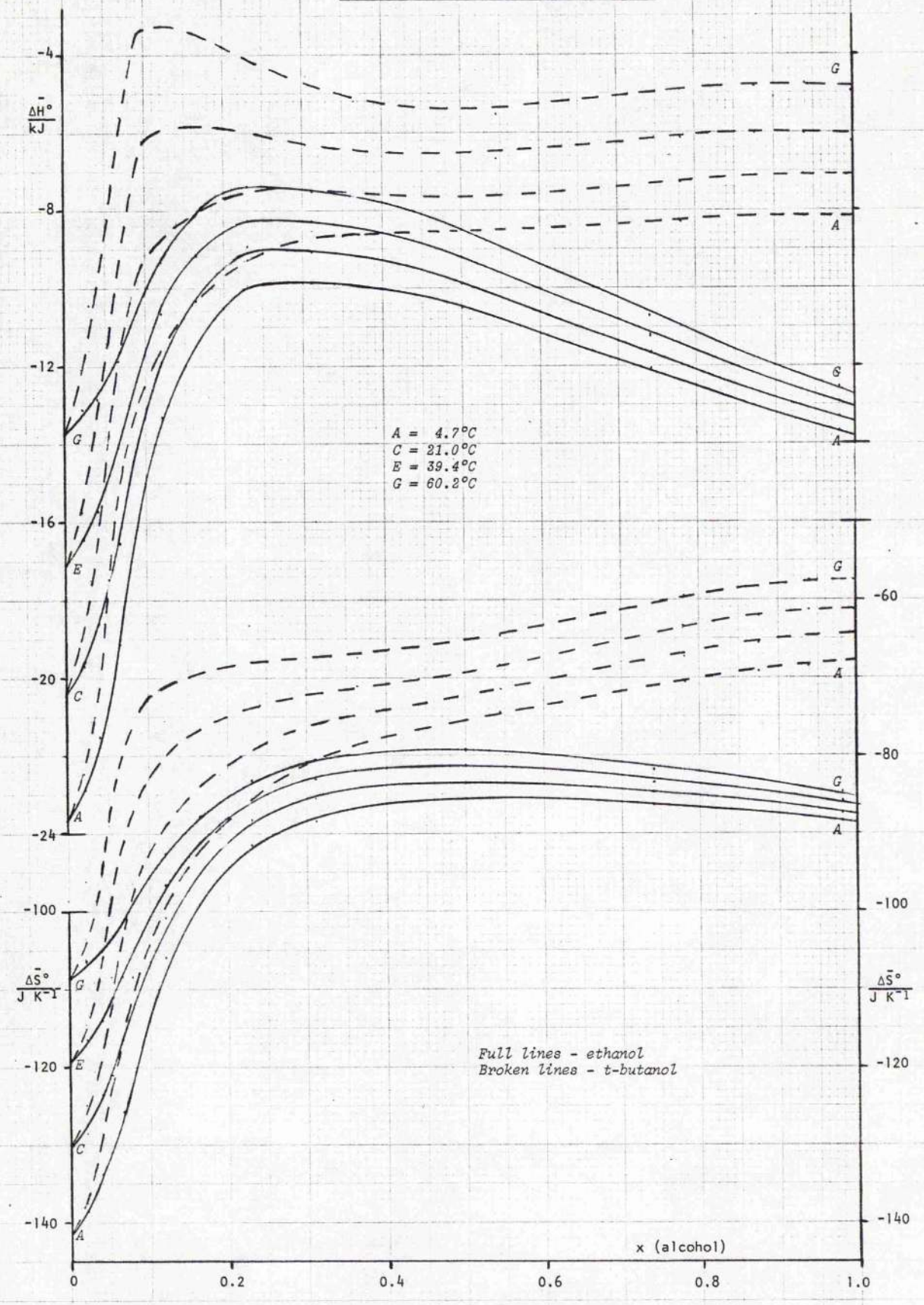
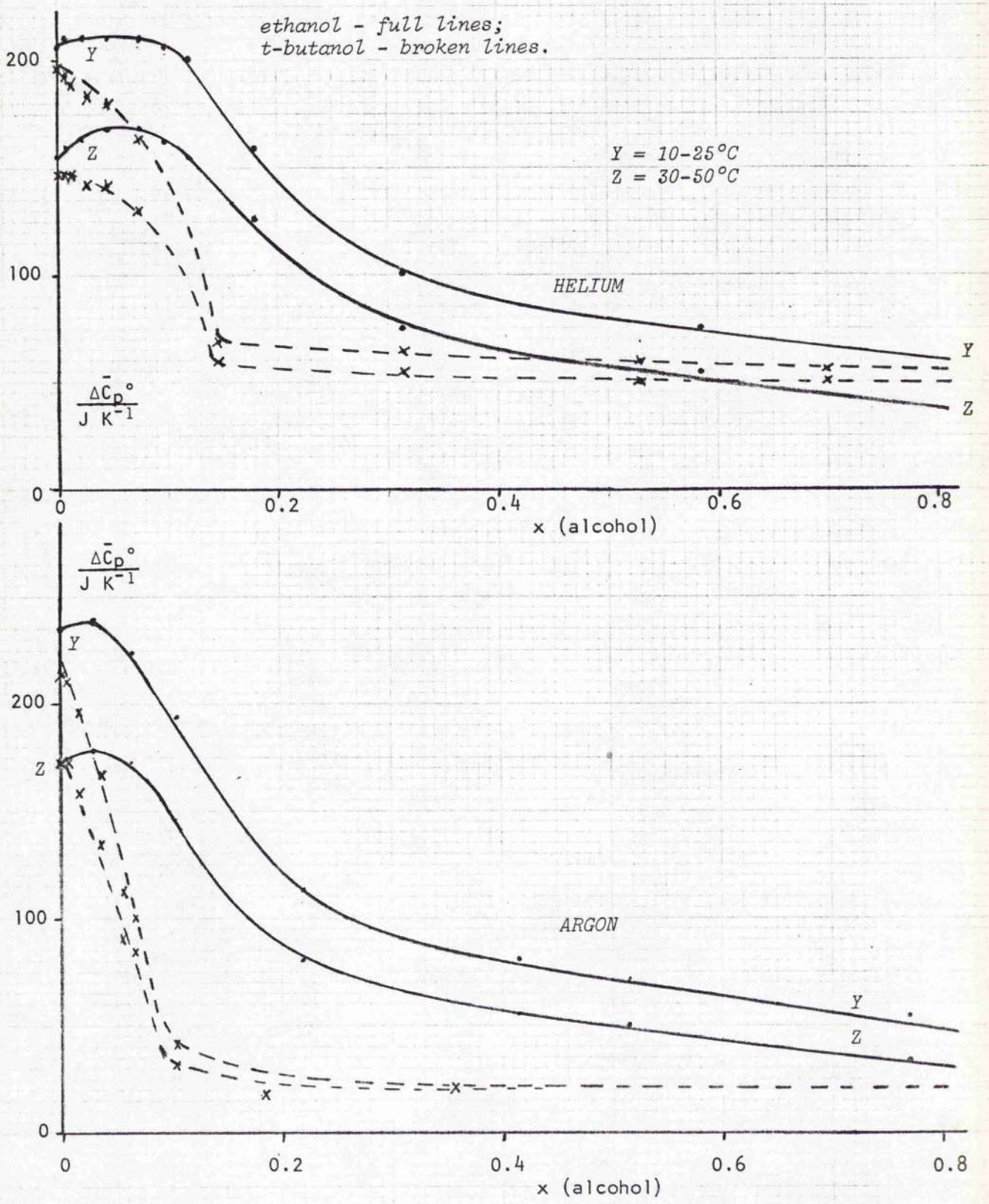


FIGURE 38 : $\Delta\bar{C}_p^\circ$ for solubility of gases in aqueous alcohols of mole fraction x:



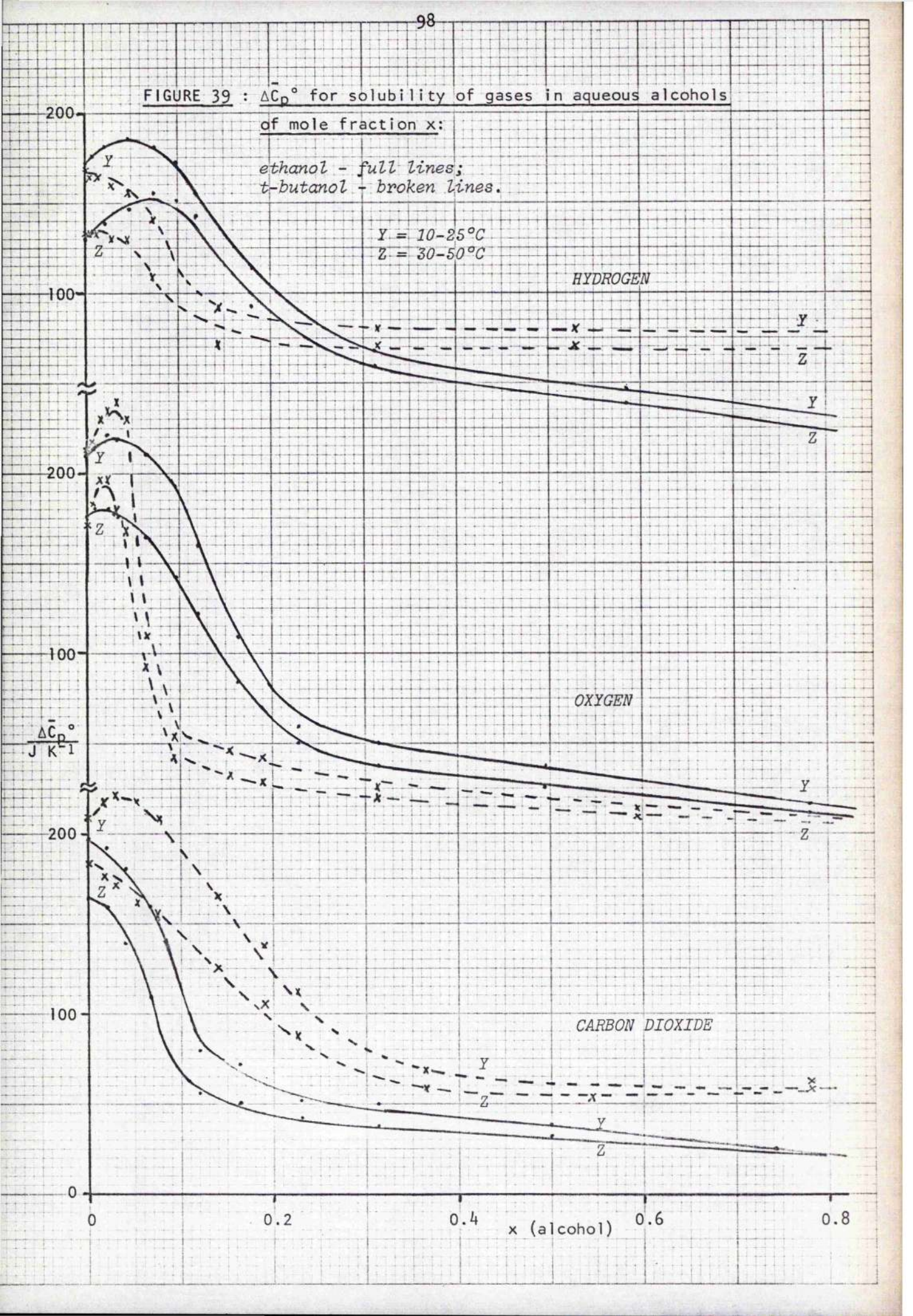


FIGURE 39 : $\Delta\bar{C}_p^\circ$ for solubility of gases in aqueous alcohols of mole fraction x:
ethanol - full lines;
t-butanol - broken lines.
Y = 10-25°C
Z = 30-50°C
HYDROGEN
OXYGEN
CARBON DIOXIDE
$\frac{\Delta\bar{C}_p^\circ}{J\ K^{-1}}$
200
100
0
0
0.2
0.4
0.6
0.8
x (alcohol)
Y
Z

2. GENERAL OBSERVATIONS

From inspection of the foregoing graphs in figures 20-39, two features are immediately apparent, which show the fulfilment of two of the objectives of this investigation.

(a) The sets of full and broken lines show exactly the same trends and changes, although at different rates; i.e. both alcohols exercise the same kind of influence on the solubility of a gas in water. The rate at which this influence is exerted depends on the nature of the alcohol, but its direction and magnitude are the same for each. *Thus a comparison between the effects of the alcohols is clearly made.*

(b) For any of the thermodynamic parameters, e.g. $\Delta\bar{H}^{\circ}$, the pattern for all of the gases is the same; i.e. each gas is affected in the same way by the addition of either alcohol. The positions on the y-axes for the different gases may be different, but the directions, rates, and magnitudes of the changes are about the same for each of them, plotted as a function of mole fraction of a given alcohol. Thus, *for monitoring the effect of an alcohol on water structure, any of the gases used is suitable,* although some may be more sensitive than others.

It is also noteworthy that the respective parameters for oxygen and argon are nearly the same throughout, and that the results for argon in aqueous ethanol correspond closely with those of Ben Naim[20] over the part of this system which he investigated. (The curves are the same shape and in fact correspond when standard states are correlated).

It therefore remains now to comment on some details of these observations, and seek their relevance to the problem of the structure of water under the headings of the effects of alcohols, the effects of temperature, and the effects of gases.

3. EFFECTS OF ALCOHOLS ON WATER STRUCTURE

(a) Variation in gas solubilities

Figures 20-27, where log s is plotted against mole fraction of alcohol, show that at lower temperatures, for each of the gases, the solubility increases slightly to a maximum (except for CO_2), then decreases noticeably to a minimum, before rising fairly steadily to its higher value for the pure alcohol. Increasing temperature smooths out these extrema until they disappear altogether in a shallow point of inflexion. Their positions are relevant to structural effects, and are summarised in the following tables derived from figures 23-27:

(i) *mole fractions for maxima:*

gas	ethanol		t-butanol	
	4.7°C	21°C	4.7°C	21°C
He	0.03	0.05	0.006	0.008
H_2	0.03	0.045	0.006	0.01
Ar	0.035	0.045	0.008	0.01
O_2	0.03	0.04	0.01	0.01
CO_2	-	-	-	-

(ii) *mole fractions for minima:*

gas	ethanol		t-butanol	
	4.7°C	21°C	4.7°C	21°C
He	0.135	0.11	0.047	0.043
H_2	0.130	0.095	0.054	0.045
Ar	0.135	0.10	0.06	0.045
O_2	0.14	0.095	0.065	0.05
CO_2	0.145	0.135	0.105	0.09

From these tables it can be seen that the positions of these extrema depend on temperature and on the alcohol, but, except for CO_2, they seem to be independent of the gas. In this section attention is focussed on the effects of the alcohols.

This same information is obtainable from figures 28-32 where $\Delta\bar{G}°$ is shown as a function of x. The extrema are of course inverted, but their positions correspond to those on the log s isotherms and show the same properties.

Now it will be recalled (see P.46) that when gas solubility is used to investigate water structure, it is usually assumed that solubility is related to the amount of organised structure in the liquid. This is because the solubility of most gases in water is accompanied by a negative $\Delta\bar{H}°$ and a negative $\Delta\bar{S}°$; i.e. the making of chemical bonds and a decrease in the disorder of the system, and therefore cluster stabilisation. When the solubility decreases, both $\Delta\bar{H}°$ and $\Delta\bar{S}°$ become less negative, i.e. less cluster stabilisation has been possible. So it is now necessary to inspect the $\Delta\bar{H}°$ and $\Delta\bar{S}°$ curves.

(b) Variation in $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$

The existence of maxima and minima on solubility isotherms depends on the kind of changes in the structure of water brought about by the alcohols. This is elucidated by reference to figures 33-37 where $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ isotherms are drawn, and the following features are seen.

(i) $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ changes correspond to one another. In fact, a Barclay-Butler plot[85] ($\Delta\bar{H}^\circ$ vs. $\Delta\bar{S}^\circ$) is linear for all the systems at low alcohol concentrations. This suggests that the same structural effects are responsible for the changes in both of these functions.

(ii) From $x = 0$ up to the positions of the maxima on the solubility isotherms, the $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ values change but slightly. So very low concentrations of alcohol do not destabilise but may even tend to stabilise the organised structure in water.

(iii) From these positions, there is a rapid and smooth change in the functions in the positive direction, until the point is reached where the curve noticeably deflects, and values remain nearly constant throughout the rest of the concentration range. (This point will hereafter be referred to as the "deflection point" in the curves). From this it seems reasonable to infer that as the alcohol concentration increases, it rapidly destabilises the structure of water, so that when a gas dissolves less bond-making and disorder decrease is possible, until at the deflection point in the curve, all the organised structure of water has disappeared.

The water-alcohol mixture then behaves "normally" over the rest of the concentration range, and the solubility of the gas in the alcohol component takes control of the thermodynamic functions. No further structural effects are possible in the system, so that $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ show no unexpected changes.

(iv) On most of the curves, this deflection point shows a temperature dependence, which is probably the same as that for the minimum in the log s isotherm, although less clearly seen here due to the larger probable error in these functions. At higher temperatures less alcohol is needed to produce the deflection point, so less of the organised structure must have been present in the water. Thus both higher temperature and alcohol molecules co-operatively decrease the total amount of organised structure in water. This is also suggested by the observation that the extent of the change in $\Delta\bar{H}^\circ$ or $\Delta\bar{S}^\circ$ from $x = 0$ up to the deflection point is inversely related to temperature. Some quantitative aspects of this temperature effect will be discussed later.

(v) For any of the gases in water, i.e. at $x = 0$, the magnitudes of $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ decrease as temperature increases. Again this suggests that increasing temperature tends to destroy the organised structure in water and so structural effects on the functions are lessened.

The conclusions suggested by these features are also supported by the $\Delta\bar{C}_p^\circ$ curves, since a positive $\Delta\bar{C}_p^\circ$ is related to the existence of hydrogen-bonded structures which can absorb energy. Figures 38-39 show that this function decreases towards zero, at the same rate as do the others, while alcohol concentration increases.

(c) Comparison between the alcohols

There is ample evidence especially in figures 23-27 for Arnett's statement (see P.7) that t-butanol exaggerates the extrema of aqueous alcohols. Also, as he found for other properties[36], the mole fraction of 0.04 is seen to be a critical one at 25°C for this alcohol. The graphs of $\Delta\bar{H}°$, $\Delta\bar{S}°$, and $\Delta\bar{C}_p°$ show, however, that this exaggeration is not due to extra structural changes, but rather a more rapid onset of these. Herein lies the key point of comparison and contrast between the two alcohols. The increase in log s occurs earlier for t-butanol in water, but is not so large; and the decrease from this maximum to its minimum is steeper and somewhat greater. Thereafter the solubilities in each mixture change similarly.

The relative positions of the extrema for the two alcohols therefore present some quantitative points of contrast. The fact that these do not occur at the same mole fraction for each alcohol shows that the structural effects are not due solely to the -OH group which is the same for both alcohols, but rather due to the alkyl groups which differ in size and shape. In support of this, Franks and Reid[29] have shown that the hydration of alcohols and of the corresponding alkanes are thermodynamically very similar, i.e. the hydrophobic part of the alcohol molecule, like an alkane, is responsible for its stabilising effect on the organised structure in water.

On this basis, a closer inspection of the maxima and minima may be carried out.

(i) The maxima on the log s curves for aqueous ethanol and t-butanol can be compared in this work, but a wider comparison is possible using Ben Naim's results for argon in aqueous methanol[19]. For argon solubility, the maxima have the following properties:

Alcohol	methanol	ethanol	t-butanol
Relative height (4.7°C)	6	3	1
Mole fraction (4.7°C)	0.05	0.03	0.006
Highest temperature	10°C	15°C	35°C

Now the existence of a maximum implies an increase of organised structure in the system. The above table therefore shows that as the alkyl group increases in size, less stabilisation of the structure is possible at 4.7°C, using less of the alcohol; but the effect persists to a higher temperature. This could mean that the smaller alkyl groups can best stabilise the larger clusters of water molecules. At the lowest temperatures the greatest proportion of these exists; so the smaller the alcohol molecule, the greater the total structure promotion at 4.7°C. On the other hand, if the larger alkyl groups can best stabilise smaller clusters, the proportion of which is smallest at lowest temperatures, then least organising effect will be shown by the largest alcohol molecules at 4.7°C. These, however, will still be able to increase organised structure at higher temperatures, where the larger clusters have ceased to exist.

This picture has been suggested rather than proved from this work. There does appear to be some correlation between the size of the alkyl group and structure stabilisation. Indeed, for the low alcohol concentration this maximum could correspond to the solubility of the appropriate alkane in water at that

temperature, where similar structural effects would operate, as was suggested by Franks and Reid[29] - see P.104.

(ii) A similar comparison of the minima could now be carried out. However, it is more relevant to compare the deflection points on the $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ curves since these are more directly related to structural changes, and can be estimated with reasonable accuracy. The deflections in $\Delta\bar{H}^\circ$ curves are sharper than those in $\Delta\bar{S}^\circ$ curves, so their positions are more accurately found and are tabulated below. For a similar reason the data for t-butanol tend to be more accurate than those for ethanol.

Mole fractions for deflection points in $\Delta\bar{H}^\circ$ curves:

gas	ethanol				t-butanol			
	4.7°C	21.0°C	39.4°C	60.2°C	4.7°C	21.0°C	39.4°C	60.2°C
He	0.3	0.3	0.3	0.2	0.15	0.12	0.1	0.07
H_2	0.3	0.2	0.15	0.15	0.15	0.1	0.06	0.04
Ar	0.22	0.22	0.22	0.22	0.12	0.11	0.08	0.07
O_2	0.24	0.22	0.18	0.16	0.10	0.09	0.08	0.07
CO_2	0.23	0.23	0.23	0.22	0.23	0.17	0.1	0.1

These deflection points, like the extrema, are seen to depend on temperature and the alcohol, but very little on the gases except carbon dioxide.

The alcohols can therefore be compared once again, incorporating Ben Naim's results for methanol[19]. For the solubility of argon, the mole fractions for the deflection points are as follows:

Alcohol:	methanol	ethanol	t-butanol
at ~5°C	0.5	0.22	0.12
at ~20°C	0.4	0.22	0.11

These mole fractions represent the quantities of alcohol required to bring about complete disappearance of an organised structure in water.

At each temperature, their ratio is about the same, i.e. approximately 4:2:1, which is also the approximate ratio of the sizes of the alkyl groups in the alcohol molecules. This suggests that the destabilising effect of alcohols on water structure is proportional to the size of their alkyl groups, i.e. to the hydrophobic nature of the molecules.

These mole fractions also correspond to the positions of minima on graphs showing heats of mixing for those alcohols in water as given by Franks and Ives[26]. At 25°C the minima occur at mole fractions of 0.32, 0.22, and 0.09 respectively, i.e. very close to the values at 20°C above, and in the same ratio. These mixing effects thus appear to have the same structural basis.

In summary, therefore, it may be concluded that the effect of an alcohol on water structure, whether for stabilising or destabilising clusters, depends on the size of its alkyl group.

4. EFFECTS OF TEMPERATURE ON WATER STRUCTURE

As on P.102 it can be assumed that where the $\Delta\bar{H}°$ and $\Delta\bar{S}°$ curves show their deflection points, structural organisation in the water has been removed by the alcohol added. So for any isotherm, the difference between the $\Delta\bar{H}°$ (or $\Delta\bar{S}°$) value at this point and its value for water depends on the amount of organisation which was originally present in water at that temperature; i.e. this $\Delta(\Delta\bar{H}°)$ or $\Delta(\Delta\bar{S}°)$ is proportional to the degree of organisation in water at the given temperature.

These data from different isotherms can therefore give a quantitative estimate of the effect of temperature on water structure.

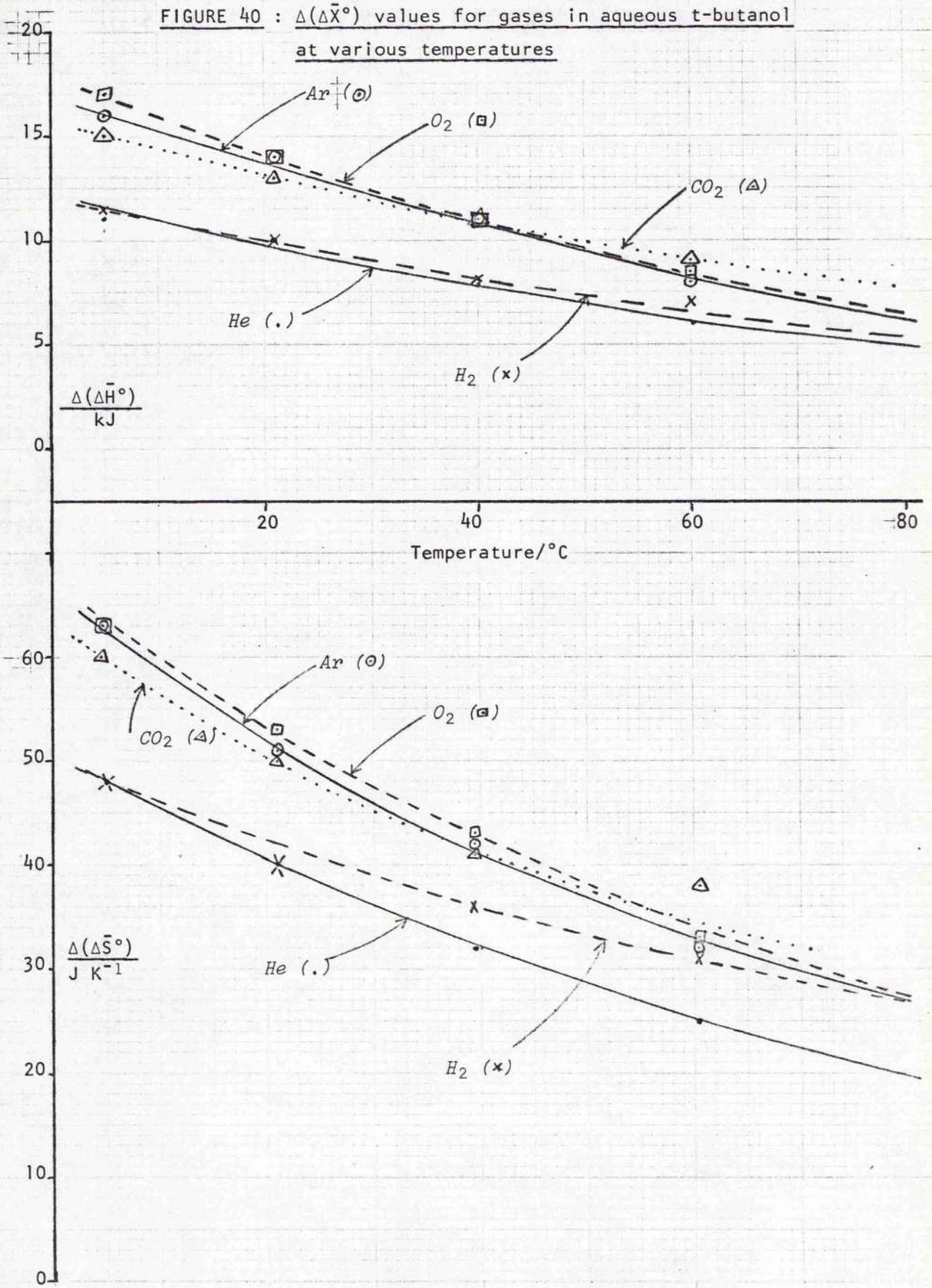
Either the ethanol or t-butanol data may be used, since both alcohols are seen to produce about the same change in $\Delta\bar{H}°$ or $\Delta\bar{S}°$ at a given temperature. The t-butanol curves, however, show the sharper deflections and so will provide the better values of $\Delta(\Delta\bar{H}°)$ and $\Delta(\Delta\bar{S}°)$, which are tabulated below, derived from figures 33-37. Also, if 4.7°C is taken for reference, where the organisation is high, then the percentage left of this structure at any other temperature is found by dividing that $\Delta(\Delta\bar{X}°)$ value by its value at 4.7°C. The average of these percentages is given in the last line of the table.

$\Delta(\Delta\bar{X}°)$ values for gases in aqueous t-butanol

Gas	$\Delta(\Delta\bar{H}°)$/kJ				$\Delta(\Delta\bar{S}°)$/J K^{-1}			
	4.7°C	21°C	39.4°C	60.2°C	4.7°C	21°C	39.4°C	60.2°C
He	11	10	7.8	6	48	40	32	25
H_2	11.5	10	8.2	7	48	40	36	31
Ar	16	14	11	8	63	51	42	32
O_2	17	14	11	8.4	63	53	43	33
CO_2	15	13	11	9	60	50	42	38
Average relative %	100	88	70	55	100	83	70	55

These values are also plotted against temperature on figure 40. This graph and the above table show again that every one of the gases behaves similarly, and that the amount of organisation in the structure of water steadily decreases as temperature increases. There is no evidence here for a transition point around 35°C as suggested by

FIGURE 40 : $\Delta(\Delta\bar{X}°)$ values for gases in aqueous t-butanol at various temperatures



Franks and Ives,[27] and other co-workers.[86-88] Also from the relative percentages and the slight curvature in the graphs it is clear that while the degree of organisation in the structure continues to decrease, it does not become zero up to the boiling-point of water (unless some unlikely transitions occur between 60°C and 100°C).

This method therefore provides reliable experimental estimates of the degree of organisation in the structure of water at different temperatures.

A few other estimates of this were presented on P.49, and the scatter among them shows how approximate they were. It is concluded from this part of the work that if the mole fraction of water with an organised structure at 5°C is 0.75, as frequently assumed, then at 20°C it is about 0.64, at 40°C about 0.53, and at 60°C about 0.41. By extrapolation, it is expected to be about 0.25 at 100°C, so that over the liquid range of water, from 0 → 100°C, the organisation of structure decreases by about two-thirds. These are significant and useful results, based on much experimental evidence.

5. EFFECTS OF GASES ON WATER STRUCTURE

(i) The relative effects which gases have on water structure can be deduced from their solubilities in water by the magnitudes of their $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ values. So if, for example, 4.7°C is taken as a reference temperature, helium has least structural effects, followed by hydrogen, then argon and oxygen very close together, with carbon dioxide having most effect. For these first four gases, the effects can again be related to the size

of the solute molecules (see also P.336 of Reference 29). For carbon dioxide, the extra large structure promotion is probably due to the ions introduced into the water by its acid-base reaction. Compared with the others this gas shows values which are only larger, suggesting that a similar mechanism operates for them all. Hydration of ions and longer range electrostatic effects will produce ordering in the system, as does the interaction of neutral gas molecules with clusters. This is consistent with mixture models outlined in Chapter 3, for which this interaction has been described as non-polar hydration. Eley[89] also showed how non-polar molecules can interact with only a limited number of sites in water, whilst ions can interact with any water molecules. Also, Frank and Evans[70] suggested that the larger the solute molecule, the more "icebergs" existed.

(ii) More informative, however, is the existence of a minimum on the solubility curve (log s vs. 1/T) for a gas, where, for the actual solution process, $\Delta\bar{H}_s$ and $\Delta\bar{S}_s$ are both zero. This is because

$$\Delta\bar{H}_s = \frac{d \log s}{d(1/T)} \qquad \text{and} \qquad \Delta\bar{S}_s = \frac{d \log s}{d \log T},$$

so that at a minimum, both functions are zero. (Also $\Delta\bar{H}_s = \Delta\bar{H}^\circ$ since the solution is ideal and $\Delta\bar{H} = 0$ for diluting the gas solution from $x = 1$ to $x = x_A$; $\Delta\bar{S}_s = \Delta\bar{S}^\circ - R \ln x_A$ since the solution is ideal and diluting the gas solution from $x = 1$ to $x = x_A$ involves $\Delta\bar{S} = R \ln x_A$. So $\Delta\bar{S}_s$ could be calculated, but need not be, since as above, $\Delta\bar{H}_s$ and $\Delta\bar{S}_s$ are both zero simultaneously.)

At the temperature of a minimum there is in the solvent some property of its structure which is critical for that gas - let us say size of clusters. At lower temperatures, $\Delta\bar{H}_s$ and $\Delta\bar{S}_s$ are both negative, i.e. the solubility of the gas promotes the organisation of structure. At higher temperatures, $\Delta\bar{H}_s$ and $\Delta\bar{S}_s$ are both positive, i.e. the solubility of the gas promotes disorganisation of structure.

Now minima are found to exist on solubility curves for water and for many of the dilute alcohol solutions, but at different temperatures. So temperature and amount of alcohol added to water are seen to affect this cluster size, and from the positions of these minima, the two effects can be related.

(a) Minima exist when $\Delta\bar{H}^\circ = 0$. So for a reference temperature of 4.7°C, from Figures 33-37, the relevant concentrations of alcohol can be found. They are listed below (x_1) along with the mole fractions for the deflection points in the $\Delta\bar{H}^\circ$ curves (x_2) for t-butanol (the data for which are more accurately obtained.) The amount of alcohol added to water has already been related to the degree of structure-breaking at a given temperature (see P.107), i.e. for x_2 in the table, 100% structure-breaking has occurred. So the ratio x_1/x_2 in the last column of the table shows the amount of structure-breaking which is critical for a given gas.

Gas	x_1 for $\Delta\bar{H}^\circ = 0$	x_2 for deflection point	x_1/x_2 (percentage)
He	0.05	0.15	33
H_2	0.075	0.15	50
Ar	0.10	0.12	83
O_2	0.08	0.10	80
CO_2	-	0.23	-

This table shows that, for example, helium cannot promote the organisation of structure if more than 33% has been destroyed. Perhaps only 33% of the clusters in water at 4.7°C are suitable for helium to stabilise. Similarly, for hydrogen the figure is 50%, for argon 83%, and for oxygen 80%. For carbon dioxide it is probably 100%. It might mean that for helium, the 67% of the clusters left, after t-butanol has caused the disappearance of the larger ones, are too small for it to stabilise; for hydrogen that 50% are too small; for oxygen and argon about 20% are too small; and for carbon dioxide none are too small. This accords with the specific interaction that carbon dioxide can have with single water molecules.

(b) Now in pure water itself, clusters will also be destroyed by increasing the temperature. So for a given gas, its critical cluster size also exists at the temperature where the curve for its solubility in water shows a minimum; i.e. for helium at 35°C, for hydrogen at 55°C, (as shown in Figures 10-13), and for oxygen at 90°C (from Himmelblau[90]).

It is therefore postulated that when the temperature has risen to 35°C, 33% of the clusters have been destroyed; at 55°C, 50% have gone; and at 90°C about 80% have gone. It is also suggested that the bigger clusters are destroyed first as the temperature rises.

These results can now be compared with those obtained in Section 4 above, in terms of the mole fraction of organised structure left at a given temperature. Again it will be assumed that at the reference temperature of 4.7°C the mole fraction of structured water is 0.75. The comparison is shown in the next table.

From Section (4)			From this section		
temperature °C	% of organised structure	Mole fraction	temperature °C	% of organised structure	Mole fraction
4.7	100	0.75	4.7	100	0.75
21	88	0.64			
39.4	70	0.53	35	67	0.5
60.2	55	0.41	55	50	0.38
			90	20	0.15

This comparison is remarkably close considering the possible errors in the parameters used in the estimations - positions of deflection points and extrema on curves which themselves may be subject to some error.

(iii) Furthermore, if it is accepted that helium stabilises the "large" clusters in water, that hydrogen stabilises the "medium" clusters, and that oxygen stabilises the "small" clusters, it is possible to estimate the relative amounts of each of these present in water at a given temperature. These amounts are shown by the magnitudes of $\Delta\bar{H}°$ for the solubility of the appropriate gases in water, as tabulated below, from Figures 33, 34, and 36; values of $-\Delta\bar{H}°$/kJ.

Temperature (approx.)	5°C	20°C	40°C
He - for large clusters	5.7	2.4	0
H_2 - " medium "	8	5.1	2.4
O_2 - " small "	16.2	12.6	9.1
Ratio of large : medium : small	0.7:1:2	0.4:1:2.5	0:1:3.8

These ratios indicate how the relative amounts of the different sized clusters change with increasing temperature: larger clusters disappear and smaller clusters increase in number. It could be that the disappearance of "large" clusters between 20°C and 40°C is related to the transition at 35°C referred to on P.108. Also the ratio for 5°C is close to that obtained on P.105 (i.e. 1:3:6) for the heights of maxima on solubility isotherms, which were also related to relative sizes of clusters.

Finally, the difference between these ratios at different temperatures is evidence for the "flickering cluster" model of Frank and Wen (see P.46). The clusters are not steady, melting uniformly say at their edges as the temperature rises, otherwise the same ratio would be maintained throughout. There is rather a continuous dynamic equilibrium between clusters of different sizes. Also, it is felt that the continuum model with its

uniform distortion of hydrogen-bonds can hardly be reconciled to this evidence.

The conclusion reached and confirmed in this section is therefore that the decrease in the organised structure of water as temperature rises is due to the progressive destruction of larger clusters.

A quantitative estimate has also been made of the total mole fractions of water organised in clusters, and of the proportions of relative sizes of clusters, at different temperatures. This is a significant contribution to the understanding of water structure.

6. A CONSISTENT MODEL FOR WATER STRUCTURE

In summary, a "flickering cluster" model is described as follows, in which a mechanism of "structure stabilisation" is presented.

An equilibrium exists between large and small clusters of water molecules, and single monomers. Clusters are subject to thermal disruption, which is minimised by the "cushioning" effect of inert solute molecules. Therefore the larger the solute molecule, the higher the equilibrium concentration of clusters in the liquid.

Also, bigger clusters can result from the collision of smaller ones. This also will be inhibited by the cushioning effect of solute molecules unless these are small enough to become enclosed within the bigger cluster, without distorting its hydrogen-bonded structure. This distortion will be proportional to the size of the solute molecules. So, for example, the small helium atom, which can easily

be fitted into the lattice structure of the icebergs, can "stabilise" large clusters by not inhibiting their formation. The bigger the solute molecule, the more inhibition of larger clusters occurs, although the total amount of structure becomes greater.

This rather simple picture of size effects is very attractive, and it is in accord with all the facts presented in this thesis.

7. FURTHER INVESTIGATIONS

Many of the conclusions reached from this investigation could be checked by further work on gas solubilities.

(i) Improvement of the $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ curves would result from more solubility determinations for the gases in the mixtures in the vicinity of the deflection points, and at the maxima in the log s isotherms.

(ii) Other aqueous mixtures could be used as solvents, e.g. with ketones, ethers, acids, urea, etc., as the organic component. More work on methanol and the propanols would be of interest. Other butanols (n-, iso-, and sec-) could be investigated to check the effect of the shape of the alkyl group on water structure. It was noticed, however, that t-butanol provided the most accurate and detailed information on structural effects, so that it ought to be used more widely.

(iii) Of the gases, helium was found to be most useful as in Section (5) above, but its low solubility sets practical limitations on accuracy. Hydrogen may be a better compromise, whilst for some parameters, oxygen appeared to give sharper changes. Rather

than select one gas, however, the present work has shown that most information is obtained by the use of a variety of gases. This variety could be increased, and thereby the postulated size effects further clarified.

APPENDIX I : Relationship of Valentiner solubility equation to thermodynamic functions

As on P.37 we have

$$\frac{d\ \ell n\ s}{dT} = \frac{\Delta\bar{H}^\circ}{RT^2}$$

$$= \frac{\Delta\bar{H}^\circ_0 + \Delta\bar{C}_p T}{RT^2} \qquad \text{from Kirchhoff's equation}$$

$$\therefore\ \ell n\ s = \int\left(\frac{\Delta\bar{H}^\circ_0}{RT^2} + \frac{\Delta\bar{C}_p}{RT}\right) dT$$

$$\therefore\ \log s = \frac{-\Delta\bar{H}^\circ_0}{2.303RT} + \frac{\Delta\bar{C}_p}{R}\log T + k \qquad \text{where } k = \text{constant}.$$

cf. Valentiner equation

$$\log s = \frac{b}{T} + c\log T - a$$

$$\therefore\ c = \frac{\Delta\bar{C}_p}{R} \qquad \therefore\ \underline{\Delta\bar{C}_p = Rc}\ ;$$

$$b = \frac{-\Delta\bar{H}^\circ_0}{2.303R} = \frac{-(\Delta\bar{H}^\circ + \Delta\bar{C}_p T)}{2.303R}$$

$$\therefore\ \underline{\Delta\bar{H}^\circ = -2.303Rb + RcT}\ ;$$

and $a = -k$.

Now $k = \log s + \frac{\Delta\bar{H}^\circ_0}{2.303RT} - \frac{\Delta\bar{C}_p}{R}\log T$

and $\log s = \frac{-\Delta\bar{G}^\circ}{2.303RT} + \log(n_B + n_C) + 4.35$ (as on P.36)

$\therefore\ k = \frac{-(\Delta\bar{G}^\circ - \Delta\bar{H}^\circ)}{2.303RT} - \frac{\Delta\bar{C}_p\, T}{2.303RT} - \frac{\Delta\bar{C}_p}{R}\log T + \log(n_B + n_C) + 4.35$

$= \frac{\Delta\bar{S}^\circ}{2.303R} - \frac{\Delta\bar{C}_p}{R}\left(\frac{1}{2.303} + \log T\right) + \log(n_B + n_C) + 4.35$

$\therefore\ -a = \frac{\Delta\bar{S}^\circ}{2.303R} - \frac{Rc}{R}\left(\frac{1}{2.303} + \log T\right) + \log(n_B + n_C) + 4.35$

$\therefore\ \Delta\bar{S}^\circ = -2.303Ra + Rc(1 + 2.303 \log T)$

$- 2.303R \log(n_B + n_C) - 2.303 \times 4.35R\ .$

APPENDIX II : Recording of Experimental Results

The following form was used to collect burette and balance readings, apply any corrections, and tabulate results to plot on the graph the line whose slope gives s'. Density and temperature are also recorded, the latter to give $\frac{1}{T}$ and also to correct s' to s.

3/12/73 — GAS SOLUBILITIES: H_2 in aqueous EtOH (4) — $x_A = 0.099$

$GAS_{ml.}$	$SOLVENT_{g.}$	$ZERO_{ml.}$	CORRECTIONS ZERO ml	CORRECTIONS PRESS. mm	GAS VOLUME ml.	SOLVENT WEIGHT g.
17.4	200	3.85	Time = 11.0 am		Flow Rate = 750	
17.2	14	.8	+.05	762	.25	14
17.0	32.5	.65	+.2		.6	33
16.7	52.5	.55	+.3		1.0	53
15.7	88.5	.85	—		1.7	88.5
15.2	302	4.1	-.25		1.95	102
14.4	55	3.9	-.05		2.95	155
13.6	89	4.05	-.2	761	3.6	189
12.75	415.5	.3	-.45		4.2	215
10.0	95.5	5.3	-1.45	760	5.95	294
9.5	531	.15	-1.3		6.6	330
9.0	56.5	.15	-1.3	759.5	7.1	355
7.7	602	.5	-1.65	759	8.05	400
7.1	26	.65	-1.8		8.5	424
4/12/73						
15.0	200	3.8	Time = 10.50 am		Flow Rate = 700	
14.9	11	.6	+.2	762	.3	11
14.3	30	.7	+.1		.8	30
14.2	40	.65	+.15		.95	40
13.55	64.5	.65	+.15		1.6	65
13.3	73.5	.6	+.2		1.9	74
12.0	319	.85	-.05		2.95	119
11.85	28	.95	-.15		3.0	128
11.4	62	.65	+.15		3.75	162
10.9	89	.5	+.3		4.4	189
9.35	430	.85	-.05		5.6	230
7.1	505	4.0	-.2		7.7	305
6.95	19	3.95	-.15		7.9	319
5.55	66.5	4.05	-.25		9.2	366
4.75	608	3.8	—	762	10.35	408

Density: (100g/20°C) 0.9658

Temperature: 30.9 °C
+273.1
T = 304.0 K
log T = 2.48229
-2.4364
$\frac{1}{T} = 32.89 \times 10^{-4}$

Solubility:
$s' = 20.2$ ml kg^{-1}
log s' = 1.3054
- 0.0465
log s = 1.2589

Time = 4.00 pm.
Flow Rate = 85 g/hr.

Density: (100g/20°C) 0.9662

Temperature: 60.3 °C
+273.1
T = 333.4 K
log T = 2.52229
-2.4364
$\frac{1}{T} = 29.99 \times 10^{-4}$

Solubility:
$s' = 25.2$ ml kg^{-1}
log s' = 1.4015
- 0.0865
log s = 1.3250

Time = 3.50 pm
Flow Rate = 81 g/hr

APPENDIX III : Deviations of Gases from Ideality

(i) Of the gases used (helium, hydrogen, argon, oxygen, and carbon dioxide) most deviation from ideal behaviour is shown by carbon dioxide, as indicated by the following molar volumes (V_m) and coefficients in the van der Waals equation $(P + \frac{a}{V^2})(V - b) = RT$.

Gas	$V_m = \frac{M}{\rho}(dm^3)$*	$a \times 10^5$ (kN m^4 mol^{-2})†	$b \times 10^5$ (m^3 mol^{-1})†
He	22.43	0.3454	2.37
H_2	22.43	2.476	2.66
Ar	22.40	13.62	3.22
O_2	22.39	13.78	3.18
CO_2	22.26	36.40	4.27

*density data from International Critical Tables, III, 3.

†values from Chemical Rubber Co. Handbook 1972, D141.

(a) Since $PV - Pb - ab/V^2 + a/V = RT$ for non-ideal gas,

deviation $\fallingdotseq a/V - Pb$.

For experimental conditions used,

$P \fallingdotseq 101.3$ kN m^{-2}, $T \fallingdotseq 300$ K, $V \fallingdotseq 22.4 \times 10^{-3}$ m^3,

and deviation $\fallingdotseq \frac{a}{22.4 \times 10^{-3}} - 101.3 \times b$.

For CO_2, this deviation is

$$\frac{36.40 \times 10^{-5}}{22.4 \times 10^{-3}} - 101.3 \times 4.27 \times 10^{-5} \text{ kN m mol}^{-1}$$

$$\fallingdotseq 1.6 \times 10^{-2} - 0.4 \times 10^{-2} \text{ kN m mol}^{-1}$$

$$= 1.2 \times 10^{-2} \times 10^3 \text{ J mol}^{-1}.$$

Also $PV = RT = 8.314 \times 300$ J mol^{-1}

$\fallingdotseq 2.5 \times 10^3$ J mol^{-1}

$\therefore$ maximum deviation $\fallingdotseq$ 0.5%.

Hence the deviations are all within the limits of experimental accuracy.

(b) This approximation to ideality also permits the use of Henry's law, and the conditions are not extreme: i.e. the minimum partial pressure of gas = 560 mmHg when total pressure is 760 mmHg. This occurs for ethanol solvent at 60°C when its vapour pressure is 200 mmHg (from Chemical Rubber Co. Handbook 1972, D147-150).

(c) In the calculation of $\Delta\bar{G}°$, the molar volume of 22.4 dm^3 is used. Again carbon dioxide shows the maximum deviation with a molar volume of 22.26 dm^3, i.e. the deviation is 0.15 dm^3 or 0.7%. But the calculation uses log V_m (= 4.350) so that the deviation in log V_m is 0.003 or <0.1%, i.e. the error is insignificant.

(ii) In the solution phase, the highest concentration is provided by carbon dioxide with $s \sim 10^3$ cm^3 kg^{-1};

i.e. no. of moles of gas in solution = $10^3/22{,}400$

i.e. $n_A < 0.05$ whilst $(n_B + n_C) \fallingdotseq 20$ to 55

i.e. concentration < 0.05 molal

and mole fraction of the gas < 0.025 or $^1/_{400}$.

Hence solutions of the gases can be regarded as ideal, because the gas molecules will be entirely surrounded by a population of solvent molecules, and solute-solute interactions will not be possible.

APPENDIX IV : Relationship between standard states for thermodynamic functions

For a gas A dissolving in a solvent mixture B + C, using the methods described in Chapter 3, equations are derived for the standard state in solution of concentration of A of 1 mol dm^{-3}, as follows:

(i) $\mu_{(soln)} = \mu^{\circ}_{(soln)} + RT \ln c$ if solution of A is dilute and ideal.

$$\therefore \Delta\mu^{\circ} = -RT \ln \frac{c}{p}$$

$$\therefore \Delta\bar{G}^{\circ} = -RT \ln\left(\frac{s}{22414} \cdot \rho\right) \quad \text{as on P.34}$$

$$\text{cf. } \Delta\bar{G}^{\circ} = -RT \ln\left(\frac{s}{22414} \cdot \frac{1}{n_B + n_C}\right)$$

$$\text{Then } \underline{\Delta\bar{G}^{\circ} = \Delta\bar{G}^{\circ} + RT \ln \rho(n_B + n_C)}.$$

e.g. (a) for $\rho = 1.0$, $(n_B + n_C) = 56$, $T = 330$ K

$$\Delta\bar{G}^{\circ} - \Delta\bar{G}^{\circ} \fallingdotseq 2.3 \times 8 \times 330 \times 1.75 \text{ J}$$

$$\fallingdotseq 9{,}000 \text{ J} ;$$

and (b) for $\rho = 0.8$, $(n_B + n_C) = 14$, $T = 280$

$$\Delta\bar{G}^{\circ} - \Delta\bar{G}^{\circ} \fallingdotseq 2.3 \times 8 \times 280 \times 1.1 \text{ J}$$

$$\fallingdotseq 5{,}000 \text{ J} .$$

(ii) $\Delta\bar{H}^{\ominus} = \frac{d}{d(\frac{1}{T})}(\frac{\Delta\bar{G}^{\ominus}}{T})$

$= -\frac{d}{d(\frac{1}{T})} R \ell n(\frac{s}{22414} \cdot \rho)$

$= -R\frac{d}{d(\frac{1}{T})} \ell n\ s - R\frac{d}{d(\frac{1}{T})} \ell n\ \rho$

cf. $\Delta\bar{H}^{\circ} = -R\frac{d}{d(\frac{1}{T})} \ell n\ s$

Then $\Delta\bar{H}^{\circ} = \Delta\bar{H}^{\ominus} + R\frac{d}{d(\frac{1}{T})} \ell n\ \rho$

or $\Delta\bar{H}^{\circ} = \Delta\bar{H}^{\ominus} - RT^2 \frac{d}{dT} \ell n\ \rho$.

---

e.g. for $T = 10°C$ $\rho = 0.96787$, $\log \rho = \bar{1}.9858$

$T = 40°C$ $\rho = 0.95168$, $\log \rho = \bar{1}.9785$

i.e. for $\Delta T = 30$ K, $\Delta \log \rho = -0.0073$

and these values are very similar for all the solvents used.

So $\Delta\bar{H}^{\circ} - \Delta\bar{H}^{\ominus} \doteq -2.3\ RT^2(-0.0003)$

$\doteq 6 \times 8\ T^2 \times 10^{-4}$ J

and for $T = 300$ K

$\Delta\bar{H}^{\circ} - \Delta\bar{H}^{\ominus} = 500$ J .

(iii) $\Delta\bar{S}^{\diamond} = -\frac{d}{dT}\Delta\bar{G}^{\diamond}$

$$\therefore \Delta\bar{S}^{\circ} - \Delta\bar{S}^{\diamond} = -\frac{d}{dT}(\Delta\bar{G}^{\circ} - \Delta\bar{G}^{\diamond})$$

$$= -\frac{d}{dT}[RT \ln \rho(n_B + n_C)]$$

$$= -RT \frac{d}{dT} \ln \rho - R \ln \rho(n_B + n_C);$$

$$\text{or } \Delta\bar{S}^{\circ} - \Delta\bar{S}^{\diamond} = \frac{(\Delta\bar{H}^{\circ} - \Delta\bar{H}^{\diamond}) - (\Delta\bar{G}^{\circ} - \Delta\bar{G}^{\diamond})}{T}$$

which also gives

$$\underline{\Delta\bar{S}^{\circ} = \Delta\bar{S}^{\diamond} - R[T \frac{d}{dT} \ln \rho + \ln \rho(n_B + n_C)]}$$

e.g. using the results in (i) and (ii) above,

$$\Delta\bar{S}^{\circ} - \Delta\bar{S}^{\diamond} \fallingdotseq \frac{500 - 9000}{330} \text{ J K}^{-1}$$

$$\fallingdotseq -25 \text{ J K}^{-1}$$

$$\underline{\text{or}} \fallingdotseq \frac{500 - 5000}{280} \text{ J K}^{-1}$$

$$\fallingdotseq -16 \text{ J K}^{-1}.$$

(iv) $\Delta\bar{C}_p^{\bullet} = \frac{d}{dT}\Delta\bar{H}^{\bullet}$

$$\therefore \Delta\bar{C}_p^{\circ} - \Delta\bar{C}_p^{\bullet} = \frac{d}{dT}(\Delta\bar{H}^{\circ} - \Delta\bar{H}^{\bullet})$$

$$= \frac{d}{dT}(-RT^2 \frac{d}{dT} \ell n\ \rho)$$

$$= -2RT \frac{d}{dT} \ell n\ \rho - RT^2 \frac{d^2}{dT^2} \ell n\ \rho$$

$$\fallingdotseq -2RT \frac{d}{dT} \ell n\ \rho$$

---

e.g. for T = 300 K, and as in (ii) above,

$$\Delta C_p^{\circ} - \Delta C_p^{\bullet} \fallingdotseq +2 \times 2.3 \times 8 \times 300 \times 3 \times 10^{-4}$$

$$\fallingdotseq 4\ J\ K^{-1}.$$

The possible error in $\Delta\bar{C}_p$ values obtained from this work is often greater than 5 J K^{-1}, so that in this case, the difference in standard states is irrelevant.

APPENDIX V : Computer Programmes

(a) FINDH : to calculate $\Delta\bar{H}^\circ$ for checking accuracy of the solubility curve:

```
FINDH;
"BEGIN" "INTEGER" N,X,T;
        "READ" N;
"BEGIN" "ARRAY" L[1:N+1,1:8,1:2];
        SAMELINE;
        "PRINT" 'CHECK    DH
  X     281.7     289.9     298.5     307.7     317.5     327.9
`;
        "FOR" T:=1 "STEP" 1 "UNTIL" 6 "DO"
        "FOR" X:=1 "STEP" 1 "UNTIL" N+1 "DO"
        "READ" L[X,T,1];
        "FOR" X:=2 "STEP" 1 "UNTIL" N+1 "DO"
        "FOR" T:=2 "STEP" 1 "UNTIL" 7 "DO"
        L[X,T,2]:=4.575*(L[X,T+1,1]-L[X,T,1])/(10-4);
        "FOR" X:=2 "STEP" 1 "UNTIL" N+1 "DO"
        "PRINT" ''L``,FREEPOINT(4),L[X,1,1],''S2``,FREEPOINT(4),
                L[X,2,2],''S2``,FREEPOINT(4),L[X,3,2],''S2``,
                FREEPOINT(4),L[X,4,2],''S3``,FREEPOINT(4),L[X,5,2],''S3``
                FREEPOINT(4),L[X,6,2],''S3``,FREEPOINT(4),L[X,7,2];
    "END";
"END";
```

Sample data and print out (for carbon dioxide in aqueous ethanol):

```
7,
46.068,0.000,0.021,0.066,0.162,0.311,0.742,0.980,
0.0036,3.160,3.148,3.093,2.984,3.162,3.516,3.642,
0.0035,3.040,3.032,2.996,2.928,3.108,3.454,3.572,
0.0034,2.930,2.926,2.906,2.872,3.057,3.392,3.502,
0.0033,2.828,2.829,2.823,2.817,3.011,3.332,3.432,
0.0032,2.732,2.741,2.747,2.763,2.968,3.272,3.365,
0.0031,2.648,2.660,2.676,2.712,2.929,3.214,3.298,
0.0030,2.570,2.588,2.611,2.664,2.893,3.158,3.232,
0.0029,2,2,2,2,2,3,3,
```

```
CHECK    DH
  X     281.7     289.9     298.5     307.7     317.5     327.9

 .0000  -5444    -5078    -4667    -4300    -3935    -3523
 .0210  -5307    -4849    -4438    -4026    -3706    -3294
 .0660  -4438    -4117    -3797    -3477    -3248    -2974
 .1620  -2654    -2516    -2379    -2242    -2105    -2013
 .3110  -2333    -2196    -2105    -2013    -1921    -1830
 .7420  -2836    -2837    -2745    -2745    -2654    -2562
 .9800  -3203    -3203    -3157    -3111    -3065    -3019
```

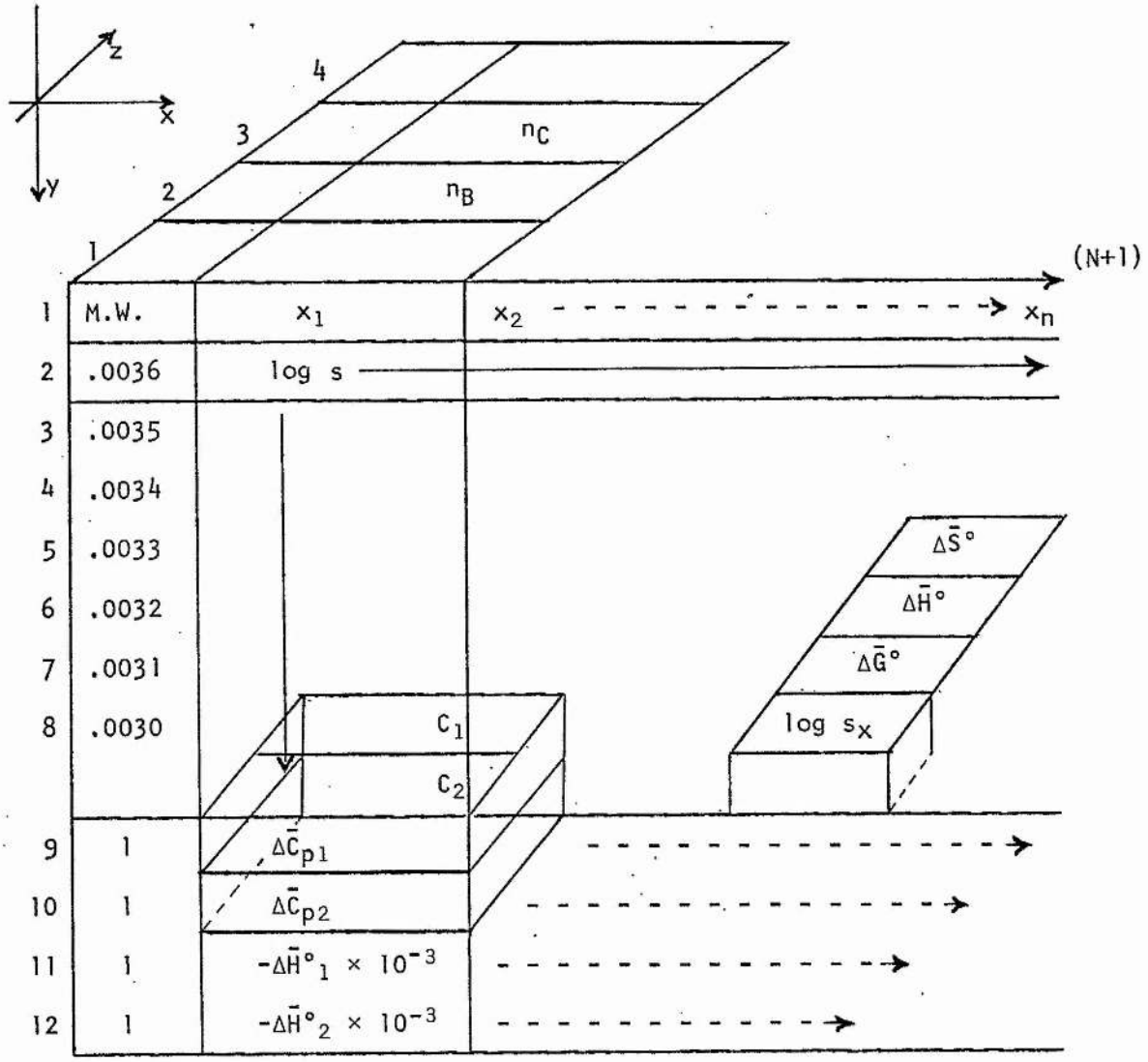
(b) DGHS21 : to calculate $\Delta\bar{G}°$, $\Delta\bar{H}°$, and $\Delta\bar{S}°$:

```
DGHS21;
"BEGIN" "INTEGER" N,X,T;
        "READ" N;
"BEGIN" "ARRAY" L[1:N+1,1:12,1:4];
        SAMELINE;
        "PRINT" '*BASIC FUNCTIONS
  X          1/T          DG(KJ)        DH(KJ)        DS(J/K)
*;
        "FOR" T:=1 "STEP" 1 "UNTIL" 12 "DO"
        "FOR" X:=1 "STEP" 1 "UNTIL" N+1 "DO"
        "READ" L[X,T,1];
        "FOR" X:=2 "STEP" 1 "UNTIL" N+1 "DO"
"BEGIN" L[X,9,2]:=-L[X,11,1]*1000-290*L[X,9,1];
        L[X,10,2]:=-L[X,12,1]*1000-310*L[X,10,1];
        L[X,1,2]:=1000/(L[1,1,1]*L[X,1,1]/(1-L[X,1,1])+18);
        L[X,1,3]:=L[X,1,1]*L[X,1,2]/(1-L[X,1,1]);
        "FOR" T:=2 "STEP" 1 "UNTIL" 4 "DO"
        L[X,T,3]:=(L[X,9,2]+L[X,9,1]/L[1,T,1])*4.184*10↑(-3);
        "FOR" T:=5 "STEP" 1 "UNTIL" 8 "DO"
        L[X,T,3]:=(L[X,10,2]+L[X,10,1]/L[1,T,1])*4.184*10↑(-3);
        "FOR" T:=2 "STEP" 1 "UNTIL" 8 "DO"
"BEGIN" L[X,T,2]:=((19.91+1.987*LN(L[X,1,2]+L[X,1,3])-4.575*L[X,T,1])/
                   L[1,T,1])*4.184*10↑(-3);
        L[X,T,4]:=((L[X,T,3]-L[X,T,2])*L[1,T,1])*1000;
        "PRINT" *'L``,ALIGNED(1,3),L[X,1,1],*'S4``,FREEPOINT(4),
                L[1,T,1],*'S7``,FREEPOINT(4),L[X,T,2],*'S7``,
                FREEPOINT(4),L[X,T,3],*'S7``,FREEPOINT(4),L[X,T,4];
                  "END";
            "END";
        "END";
"END";
```

Sample data (for carbon dioxide in aqueous ethanol):

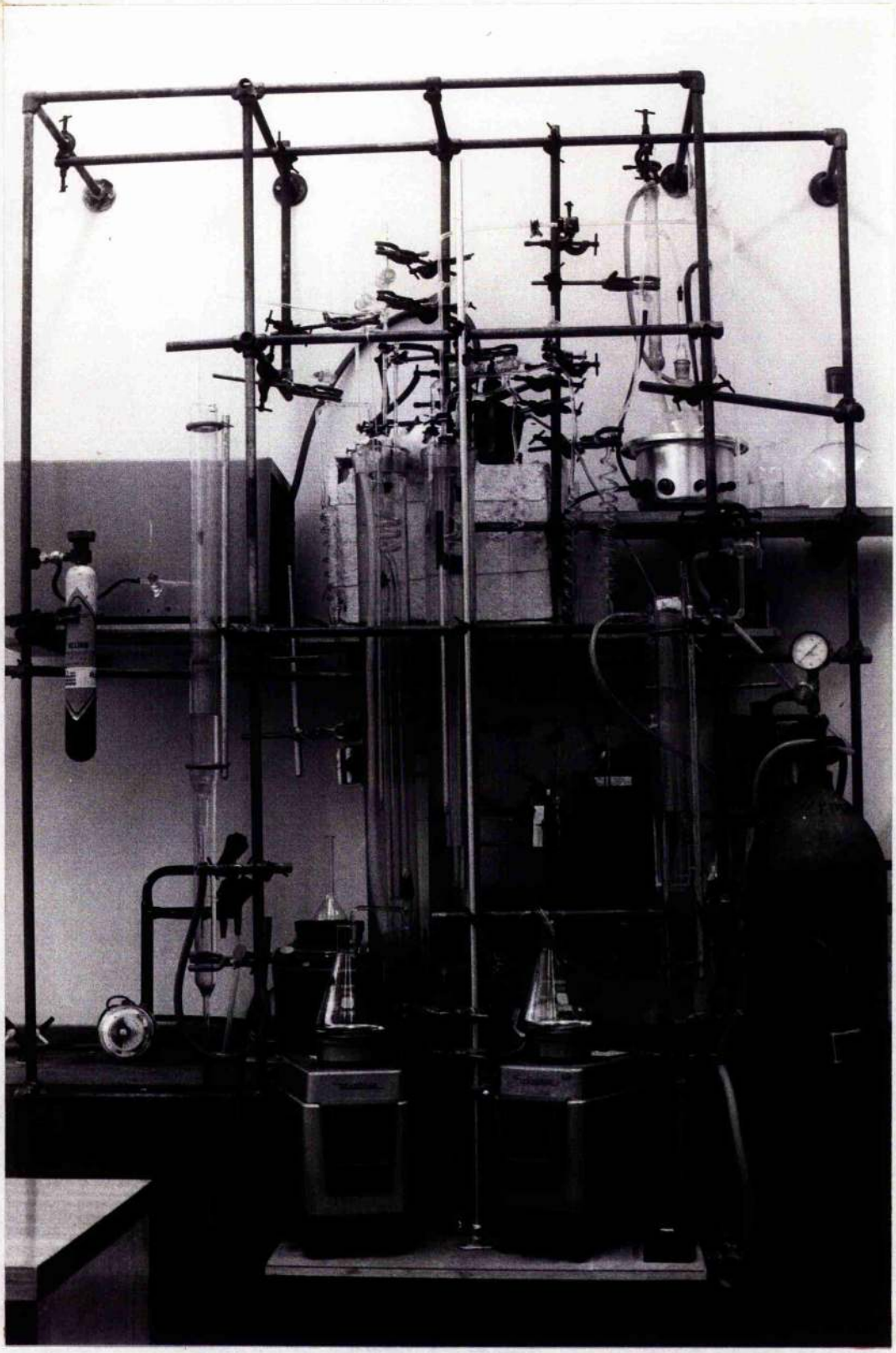
```
11,
46.068,0.000,2.021,4.066,6.162,8.311,8.742,8.983,8.648,8.128,8.230,8.509
0.0036,3.164,3.145,3.093,2.984,3.161,3.516,3.642,3.130,2.997,3.051,3.347
0.0035,3.041,3.033,2.996,2.926,3.110,3.454,3.572,3.021,2.930,3.003,3.298
0.0034,2.930,2.926,2.906,2.871,3.062,3.392,3.502,2.928,2.866,2.952,3.241
0.0033,2.828,2.828,2.823,2.819,3.016,3.338,3.433,2.827,2.806,2.906,3.191
0.0032,2.734,2.738,2.747,2.770,2.972,3.278,3.365,2.741,2.749,2.862,3.147
0.0031,2.645,2.656,2.676,2.724,2.930,3.214,3.298,2.662,2.695,2.825,3.095
0.0030,2.571,2.583,2.611,2.680,2.890,3.156,3.232,2.591,2.644,2.788,3.045
1,47,46,38,17,12,6,4,43,21,14,9,
1,39,38,26,12,9,6,4,33,15,10,8,
1,5.07,4.9,4.12,2.54,2.21,2.8,3.21,4.62,2.93,2.20,2.40,
1,4.19,4.02,3.43,2.22,2.0,2.7,3.1,3.84,2.58,2.60,2.22,
```

Both these programmes use an array where the data is presented in the (x,y) plane, and the appropriate results are calculated into the (y,z) plane; e.g. for DGHS21, the structure is as follows:



The programme FINDH actually uses part of this same data with x = (1 → N+1), y = (1 → 8) and z = (1 → 2).

APPENDIX VI : Photograph of gas solubility apparatus



REFERENCES

1. W. Henry; Phil. Trans. Roy. Soc. (London) 1803, 29, 274.
2. R. Battino & E. Wilhelm; Chem. Rev. 1973, 73, 1.
3. R. Battino & H.L. Clever; Chem. Rev. 1966, 66, 395.
4. T.J. Morrison & F. Billett; J.C.S. 1948, 2033.
5. F.M. Raoult; Comptes Rendu 1887, 104, 1430;
   Z. physik chem. 1888, 2, 353.
6. J.H. Hildebrand; J.A.C.S. 1929, 51, 66.
7. J.H. Hildebrand, J.M. Prausnitz, & R.L. Scott; "Regular and Related Solutions", 4th Edn. 1970, ch. 8.
8. T.J. Morrison & N.B.B. Johnstone; J.C.S. 1954, 3441.
9. A. Lannung; J.A.C.S. 1930, 52, 68.
10. J.T. Ashton, R.A. Dawe, K.W. Miller, E.B. Smith, & B.J. Stickings; J.C.S. (A) 1968, 1793.
11. T.J. Morrison; J.C.S. 1952, 3814.
12. T.J. Morrison & F. Billett; J.C.S. 1952, 3819.
13. T.J. Morrison & N.B.B. Johnstone; J.C.S. 1955, 3655.
14. S. Valentiner; Z. Physik 1927, 42, 253.
15. A. Ben-Naim; J. Phys. Chem. 1965, 69, 3240.
16. A. Ben-Naim; J. Phys. Chem. 1965, 69, 3245.
17. A. Ben-Naim & M. Egal-Thal; J. Phys. Chem. 1965, 69, 3250.
18. A. Ben-Naim; J. Phys. Chem. 1967, 71, 1137.
19. A. Ben-Naim; J. Phys. Chem. 1967, 71, 4002.
20. A. Ben-Naim & S. Baer; T.F. Soc. 1964, 60, 1736.
21. A. Ben-Naim; J. Phys. Chem. 1968, 72, 2998.
22. A. Ben-Naim & G. Moran; T.F. Soc. 1965, 61, 821.

23. A. Ben-Naim; J. Phys. Chem. 1965, 69, 1922.

24. A. Ben-Naim; "Water and Aqueous Solutions" (Ed. Horne) 1972, ch. 8 & ch. 11.

25. A. Ben-Naim; "Water, a Comprehensive Treatise" (Ed. Franks) vol. 1, 1972, ch. 11, & vol. 2, 1973, ch. 11.

26. F. Franks & D.J.G. Ives; Q. Rev. Chem. Soc. 1966, 20, 1.

27. F. Franks & D.J.G. Ives; J.C.S. 1960, 741.

28. F. Franks & B. Watson; T.F. Soc. 1967, 63, 329.

29. F. Franks & D.S. Reid; ref. 25, vol. 2, 1973, ch. 5.

30. P. Schläpfer, T. Audykowski, & A. Bukowiecki; Schweiz Arch. Angew. Wiss. Tech. 1949, 15, 299.

31. C.B. Kretschmer, J. Nowakowska, & R. Wiebe; Ind. Eng. Chem. 1946, 38, 506.

32. M. Roche; Inds. Agr. Aliment (Paris) 1948, 65, 127.

33. J. Pospisil & Z. Luzny; Collection Czech. Chem. Commun. 1960, 25, 589.

34. Chemical Rubber Co.; "Handbook of Chemistry & Physics" 1970-71, 51, F191.

35. E.M. Arnett & D.R. McKelvey; J.A.C.S. 1965, 87, 1393, 1541 & J.A.C.S. 1966, 88, 5031.

36. E.M. Arnett; "Physico-Chemical Processes in Mixed Aqueous Solvents" (Ed. Franks) 1967, ch. 6, p117.

37. W. Kauzmann; Advances in Protein Chem. 1959, 14, 1.

38. G. Némethy & H.A. Scheraga; J. Chem. Phys. 1962, 36, 3382, 3401.

39. L. Pauling; Science 1961, 134, 15.

40. A.E. Markham & K.A. Kobe; Chem. Rev. 1941, 28, 519.

41. R.W. Bunsen; Ann. chim. phys. 1855, 43, 496.

42. W. Ostwald; "Manual of Physico-Chemical Measurements" (Macmillan Co. London 1894), 172.

43. D.D. Van Slyke & J.M. Neill; J. Biol. Chem. 1924, 61, 523.

44. H.P. Cady, H.M. Elsey, & E.V. Berger; J.A.C.S. 1922, 44, 1456.

45. J.L.R. Morgan & A.H. Richardson; J. Phys. Chem. 1930, 34, 2356.

46. J. Horiuti; Sci. Papers Inst. Phys. Chem. Res. Tokio, 1931, 17, 125.

47. C.E. Klots & B.B. Benson; J. Chem. Phys. 1963, 38, 890.

48. C. McAuliffe; J. Phys. Chem. 1966, 70, 1267.

49. D.S. Buell & J. Eldridge; J. Chem. Data 1962, 7, 187.

50. W.R. Grimes, N.V. Smith, & G.M. Watson; J. Phys. Chem. 1958, 62, 862.

51. E.H. Denton, S.C. Lucero, & L.O. Roellig; Rev. Sci. Instr. 1962, 33, 1467.

52. G. Burrows & F.H. Preece; J. Appl. Chem. (London) 1953, 3, 451.

53. H.L. Friedman; J.A.C.S. 1954, 76, 3294.

54. A. Ben-Naim & S. Baer; T.F. Soc. 1963, 59, 2735.

55. M.W. Cook & D.N. Hanson; Rev. Sci. Instr. 1957, 28, 370.

56. J.H. Hildebrand & L.W. Reeves; J.A.C.S. 1957, 79, 1313.

57. C.E. Klots & B.B. Benson; J. Marine Res. 1963, 21, 48.

58. P.F. Scholander; J. Biol. Chem. 1947, 167, 235.

59. E. Douglas; J. Phys. Chem. 1965, 69, 1608.

60. J.H. Hildebrand & J.H. Dymond; Ind. Eng. Chem. Fundamentals, 1967, 6, 130.

61. H.L. Clever, R. Battino, J.H. Saylor, & P.M. Gross; J. Phys. Chem. 1957, 61, 1078.

62. J.H. Saylor & R. Battino; J. Phys. Chem. 1958, 62, 1334.

63. H. Koenig; Z. Naturforsch. 1963, 18a, 363.

64. J.Y. Buchanan; Proc. Roy. Soc. (London) 1874, 22, 192, 483.

65. A. Leduc; Compt. Rendu. 1906, 142, 149.

66. D.D. Eley; T.F. Soc. 1939, 35, 1281.

67. H. Frank; ref. 25, vol. 1, 1972, ch. 14.

68. H.M. Chadwell; Chem. Rev. 1927, 4, 375.

69. A. Eucken; Nachr. Akad. Wiss. Göttingen 1946, p38.

70. H.S. Frank & M.W. Evans; J. Chem. Phys. 1945, 13, 507.

71. J.A.V. Butler; T.F. Soc. 1937, 33, 235.

72. A. Ben-Naim; T.F. Soc. 1970, 66, 2749.

73. H.S. Frank & W.Y. Wen; Disc. F. Soc. 1957, 24, 133.

74. L. Pauling; "The Nature of the Chemical Bond", 3rd edn., p472.

75. H.S. Frank & A.S. Quist; J. Chem. Phys. 1961, 34, 604.

76. G. Wada; Bull. Chem. Soc. Japan 1961, 34, 955.

77. H.S. Frank & F. Franks; J. Chem. Phys. 1968, 48, 4746.

78. D.H. Everett; D.D. Eley; Disc. F. Soc. 1957, 24, 216-219.

79. K. Buijs & G.R. Choppin; J. Chem. Phys. 1963, 39, 2035, 2042.

80. J.D. Bernal & R.H. Fowler; J. Chem. Phys. 1933, 1, 515.

81. J.A. Pople; Proc. Roy. Soc. 1951, A205, 163.

82. J.D. Bernal; Proc. Roy. Soc. 1964, A280, 299.

83. D. Eisenberg & W. Kauzmann; "The Properties and Structures of Water" (Oxford Press) 1969, ch. 5.

84. J.H. Hildebrand & K.W. Miller; J.A.C.S. 1968, 90, 3001.

85. I.M. Barclay & J.A.V. Butler; T.F. Soc. 1938, 34, 1445.

86. F.S. Feates & D.J.G. Ives; J.C.S. 1956, 2798.

87. S.R. Gupta, G.J. Hills, & D.J.G. Ives; Disc. F. Soc. 1957, 24, 147.

88. F. Franks, M. Gent, & H.H. Johnson; J.C.S. 1963, 2716.

89. D.D. Eley; T.F. Soc. 1944, 40, 184.

90. D.M. Himmelblau; J. Phys. Chem. 1959, 63, 1803.